ELAEIS GUINEENSIS

AFRICAN OIL PALM
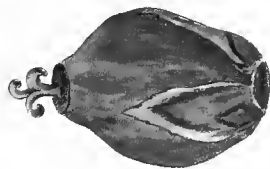
SINGLE FRUIT
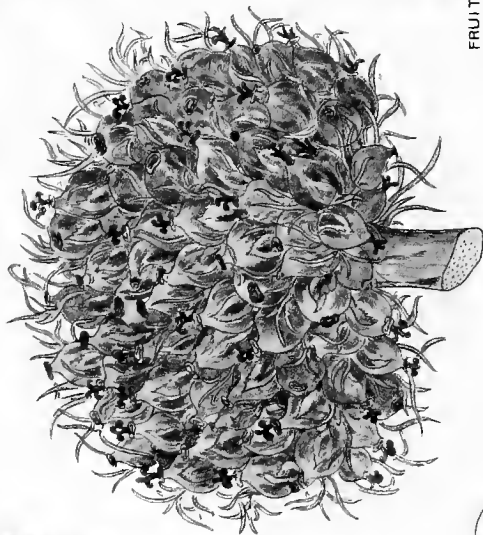
KERNELS
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FRUITING HEAD
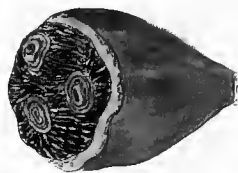
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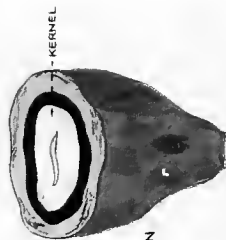
FRUIT IN SECTION

KERNEL

FATTY FOODS

THEIR PRACTICAL EXAMINATION

A HANDBOOK FOR THE USE OF ANALYTICAL AND TECHNICAL CHEMISTS

BY

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PREFACE

In no department of analytical chemistry is greater difficulty experienced than in that which deals with the examination of natural food-products. Of these food-products perhaps none present so much diversity in natural composition as do the oils and fats. This diversity of character, combined with a marked similarity of constitution, and, in consequence, bearing with it the greatest difficulty of resolution, has made the analysis of oils and fats both prolific of method and uncertain in result. Unfortunately the wide variations which pure oils and fats show in *rare* instances are often made so much of that a feeling of great uncertainty is raised in the mind of the more casual investigator as to the reliance he may put on the analytical indications to be obtained—a feeling which would not be shared by the expert in the field.

We have, therefore, endeavoured to present certain methods of examination of edible oils and fats and such technical details as are necessary for their interpretation in a more concise and definite manner than that in which they are usually treated, passing over as much as possible those rare exceptions with which the investigator may be never faced.

Out of the vast host of analytical methods for arriving

at, not only various ends, but also the same end, we have made a selection which experience has shown us are those which will arrive at satisfactory solutions in the great majority of cases. We have, as a rule, given only one method of achieving a certain result, and if the reader, whether critic or expert, should not therefore find some method, which he consequently thinks has been omitted through ignorance, it is sufficient to say that omission of a method may often be better evidence of the knowledge of it than its presentation. Nor does there seem the slightest use in preserving methods and ideas which, however efficient they have been in their time, have become superseded or unnecessary. The progress of analytical chemistry is not served either by a foolish clinging to obsolete methods or by the elaboration of new ones which are supererogatory. To some no arrangement or advice or scheme would be satisfactory or free from objection, and with them this book has no concern.

To the more humble investigator in this difficult field we desire to present the results of many years' experience, with the hope that methods and ideas which have brought success to the authors may enable him also to elucidate the problems with which he may have to grapple, though we cannot lay too much stress on the fact that scientific and skilled adulteration has sounded the death-knell of rough and ready methods of examination.

We desire to express our indebtedness to Mr. Francis H. Loder for procuring for us various commercial specimens of nuts and seeds, and of the oils and fats

obtained from them, and also for some helpful suggestions.

We are indebted to Dr. R. Vincent, Senior Physician to, and Director of, the Bacteriological Laboratory at the Infants' Hospital, Vincent Square, S.W., for the photographs of bacteria, etc., in the section on Milk.

Our thanks are due to Messrs. Baird & Tatlock (London), Ltd., for making the special extraction apparatus described on p. 11, and for the use of the block for the purpose of illustration.

The Director of the Royal Botanic Gardens, Kew, has kindly allowed us to sketch some of the fruits and seeds which were not in our possession, and Mr. J. Masters Hillier has courteously facilitated this work.

We also desire to thank Mr. T. Macara for his kindness in allowing us to include his hitherto unpublished and most valuable work on the use of the " levigation " process in the analysis of cocoa, etc.

Our greatest thanks, however, are due to Miss Enid M. Jesson, not only for the original drawings of various fruits and oil-bearing seeds, etc., but for all the labour entailed in the preparation of the MSS. for publication. We feel that without her aid this book in all probability would have fallen far short of that usefulness which we trust it will attain.

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E. RICHARDS BOLTON.
CECIL REVIS.

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    LONDON, W.

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ERRATA

Page 15, 3rd figure in 1st column of table, " + 6 " should read " − 6."

Page 31, 1st line, " 3 grm." should read " 1 grm."

Page 177, title of page, " **Malabar** " should read " **Mafura**."

FATTY FOODS

CHAPTER I.

GENERAL INTRODUCTION.

In the following chapters the examination of fatty foods is regarded purely from the *edible* standpoint. It must be clearly understood that only the properties of the various oils, etc., are considered, which come within that purview. As a consequence, the treatment is somewhat one-sided, but the edible oil industry has undergone such enormous development of late years, that it has become, for certain purposes, especially that of margarine manufacture, quite possible to regard oils and fats from the point of view of that industry only, and to supply all the necessary information to those engaged in such work, without treating of the various other purposes to which the same oils may be put.

This method of treatment has been adhered to in every particular, with one or two slight exceptions in which the divergence seemed justified.

The analytical methods here given for the practical examination of fatty foods presuppose a sufficient knowledge of the chemistry of fats and oils, and this

knowledge is therefore tacitly assumed, but, if information be required in this direction, the reader is referred to such a standard text-book as *Oils, Fats and Waxes*, by Dr. J. Lewkowitsch.

No attempt has been made to cover the whole of the field which to-day must be included under the title, but simply to place in the hands of those not intimately acquainted with the subject, such analytical methods and hints as to their interpretation, as will enable the casual investigator in the field to arrive at satisfactory conclusions regarding the more ordinary fatty foods which may come before him. There is no pretence of covering the whole field of analytical methods which have been, and are employed in such investigations ; but those methods, which from long experience the authors consider in the vast majority of cases both reliable and sufficient, are given in such a detailed form that the performance of them, under strict adherence to the description laid down, will produce similar analytical figures to those which they themselves obtain.

In the examination of fatty foods it is necessary to consider—

(1) The object of the analysis.

(2) The analytical methods to be employed; and then to pass to—

(3) The interpretation of the results obtained ; for which purpose it is necessary to have—

(4) Typical analytical data for the substances dealt with, and descriptions of their source and origin.

Object of Analysis.

I. Oils and Fats (*per se*).

The examination of these is undertaken in order to determine—

(1) *Their purity, i. e.* their freedom from other

fats, oils, waxes and substances not natural to them.
In the case of simple oils and fats, this may in many
cases present no great difficulty, but when complex
mixtures of two or more different fatty substances
are the subject of the investigation, it is not too much
to say that the interpretation of results can only
be characterised as careful and systematic scientific
guesswork, in which the experience of the analyst plays
a part equally as great as that of his analytical skill.
In many cases, on the other hand, particularly those of
direct substitution, the deductions may be made with
as great certainty as with any other type of analysis.
Under the heading of purity will come also determina-
tions of *moisture, non-fatty impurities, metallic con-
taminations* and *artificial colouring matters.*

(2) *Their suitability for technical purposes.*

To give an answer to such a question as " suitability "
for a certain purpose, will generally require technical
knowledge and experience, but to deal with this is
outside the scope of this work, and it is only possible
to indicate the kind of question which may be asked.
When, however, a definite question is put, it is often
the case, that the exercise of common-sense and reference
to the properties of the substance under consideration
will help, even the inexperienced, to give a satisfactory
reply.

The problems which may arise are :

(*a*) The matching of one oil or fat, or a mixture of
such substances, by some other oil or fat or mixture,
which in general properties and behaviour will enable
it to be used as a substitute. Such cases would arise
with biscuit and cake fats, cocoa-butter substitutes, etc.
It is needless to say that the substitute must be cheaper
than the real article.

(*b*) The comparison of deliveries with samples sup-

plied. This is often an easy task, but in many cases will require very careful examination to avoid substitutes.

(c) The investigation of competitive articles, such as, the precise nature of the mixtures used in similar processes by different manufacturers.

(d) The possibility of cheapening a manufacturing process or article by the use of new oils and fats.

In giving an opinion on these points it will be necessary to gather all the information possible as to (1) *The keeping properties of the oils and fats* which it is proposed to use, under the conditions to which they are to be exposed. For instance, a fat which would be possible for a certain purpose if used alone, might, from its likelihood of becoming rancid, or of being easily attacked by mould, be quite unsuitable if mixed with protein materials. (2) *The consistency of mixtures of oils and fats,* and their consequent behaviour at temperatures to which they will be exposed. Consistency, however, is not a simple function of the melting and solidifying points. It is rather a question of physical characteristics, and the result of the formation of eutectic compounds. This must be carefully remembered, for the addition of a high melting-point fat to a low melting-point fat does not always result in an intermediate mixture, as the melting-point of the mixture may be below that of the more fusible component until a considerable addition of the other has been made. It is necessary also to distinguish between *brittle* fats and *plastic* fats. Brittleness may be overcome sometimes by small additions of other fats (which may have to be looked for very carefully), or it may be got rid of by mechanical treatment only. (3) *Digestibility :* To this there is no adequate means of reply. It is usually taken that ease of saponification and digestibility are synonymous terms,

but it is very doubtful if they are really so. (4) *The presence of poisonous substances :* These may arise either from (*a*) the fat itself—such as in castor, croton, chaulmugra oils etc.; or from (*b*) the process of manufacture, such as contaminations from copper, arsenic and other injurious metals, as well as from organic substances. Some vegetable oils and fats in their crude state may, on account of the presence of cyanogenetic glucosides in the original seed, etc., contain appreciable quantities of prussic acid, which is, however, never likely to be found in the refined oil. (5) *Taste and smell :* While some oils or fats are valued for the presence of a characteristic taste or smell, others are judged by the absence of these. Information may often be required as to whether it would be possible to permanently render an oil entirely tasteless or odourless, or whether, on the other hand, a desired taste or smell may be enhanced, or is of such an intensity as should be reasonably expected. This, however, requires a technical knowledge of the processes used in oil refining. (6) *Colour :* It is often necessary to determine whether the colour is natural or artificial, and in those cases in which the colour is objectionable, it may be necessary to say whether it can be removed or improved.

In Chapter V, dealing with the various fats and oils, the above properties will be given as far as possible.

II. Fatty Foods.

In the examination of these substances in which the oil or fat only appears as a constituent, it will be necessary to determine :

(*a*) *The content of fatty matter,* and in many cases whether it be natural to the food, and, if not natural,

whether suitable or prejudicial to the nature and use of the food.

(b) *The content of non-fatty constituents;* in which case it may be necessary only to determine these quantitatively under certain arbitrary headings, or in certain special cases their actual nature may be required.

(c) *In the case of faulty products,* whether the fault lies with the fat or the non-fatty constituents.

CHAPTER II.

GENERAL ANALYTICAL METHODS.

IT is unfortunately too often assumed that the analysis of fatty materials is of a rough and ready character, but it cannot be too clearly understood that the utmost possible precision, not only of the analytical procedure, but also in the preparation and standardisation of the reagents and instruments employed, is absolutely necessary in such analysis. For this reason all burettes, pipettes and measuring vessels of any kind should be carefully checked by the analyst under the conditions of his own work, though on account of the difficulty of checking instruments of large capacity, it is advisable to obtain these certified, either at the National Physical Laboratory or at Charlottenburg, and to bring all other apparatus into line with these by actual weighing. (1 c.c. = 0·99807 grm. weighed with brass weights in air at 60° F.). Similarly in the case of the standardisation of solutions, such standardisation should be carried out against solutions of the same normality. For instance N/10 acid should be standardised against N/10 alkali directly made up, and not against a solution made by diluting the normal strength ten times, and so on.

The necessity of these precautions will be understood when we consider the high molecular weights involved in fat analysis. In these days of yearly publication of revised atomic weights, care must be taken to employ

the same figures for all purposes.   For instance, in cal-
culating nitrogen, analysts invariably employ 14 as the
atomic weight of nitrogen, but will at the same time
calculate N/H_2SO_4 as containing 49 grm. per litre
(instead of 49·04).

Preparation of Sample for Analysis.

CASE 1 : FAT OR OIL *per se*.—The sample must
(if necessary) be brought into the liquid condition at
the lowest possible temperature, and if then clear
and bright, the analysis of it may be proceeded with
forthwith.   Turbidity may be due to suspended
matters or moisture, and in either case filtration through
thick soft filter-paper should be resorted to until a
clear and bright filtrate is obtained.   The filtration
should be carried out at a temperature sufficiently
high to keep the whole of the fat in a melted
condition, any obvious water being allowed to settle out
before pouring on the filter.   While any good thick
soft filter-paper will serve the purpose, we strongly
recommend C.S. and S. No. 604.

CASE 2 .   OLEAGINOUS MATERIALS.—In this case the
fat will have to be extracted after suitable preparation
of the material.   Great care must be exercised in
adopting a method of disintegration suitable to the
nature of the sample under examination.

(*a*) Materials of comparatively low fat content, if of
a friable nature and not obviously greasy, may be
ground in a coffee mill, or even with a pestle and
mortar.   Precaution must be taken that the whole of
the material passes through, as in the case of certain
substances portions which are of a less friable nature
may be left in the mill.   In all cases a sufficiently

large portion should be ground to produce a fair average sample. The ground sample should be *immediately* transferred to a stoppered bottle.

(*b*) Materials of high fat content have to be carefully handled, as a small amount of pressure may cause portions of the fat to be exuded. In many of these cases a shredding machine, such as is used for vegetables, should be employed, or it may even be necessary to commence extraction without any preliminary disintegration. It is undoubtedly due to faulty methods of shredding that figures are published as representing the average fat content of such substances as copra, which to any oil miller are obviously absurd. In mill operations, a slight error in the fat content of a sample, caused either by faulty disintegration or extraction, may cause apparent loss or gain of many tons of fat in a short period.

Extraction and Estimation of the Oil or Fat.

The only satisfactory method (with certain rare exceptions) is a continuous extraction by means of a volatile solvent. For this purpose the authors prefer light petroleum spirit boiling below 40° C., as this solvent extracts a pure fat where in many cases methylated ether would extract non-fatty substances as well as the fat. The ordinary Soxhlet extractor may be used, but the form shown in the sketch (Fig. 1) is more efficient, economical of solvent, and rapid, and has been employed for many years by the authors for a very large number of extractions carried out in a routine manner, but requiring at the same time a high degree of accuracy. The fitting up of the extractor will be seen from the sketch. The outer tube is indented about two inches above the

neck in order to carry the extractor proper, which is lightly plugged at its lower end with cotton-wool, and has a disc of filter-paper resting on the wool, to prevent the material to be extracted passing into the wool. The lower end of the extractor just enters a folded filter placed in the neck of the outer tube. The quantity of solvent used should not be sufficient to fill the extraction tube when working. The flask should be sunk to the shoulder in a water-bath, which may be safely and efficiently heated by means of a 16 c.p. electric lamp, partially submerged in the water, and as rapid a rate of flow is maintained as is consistent with safety.
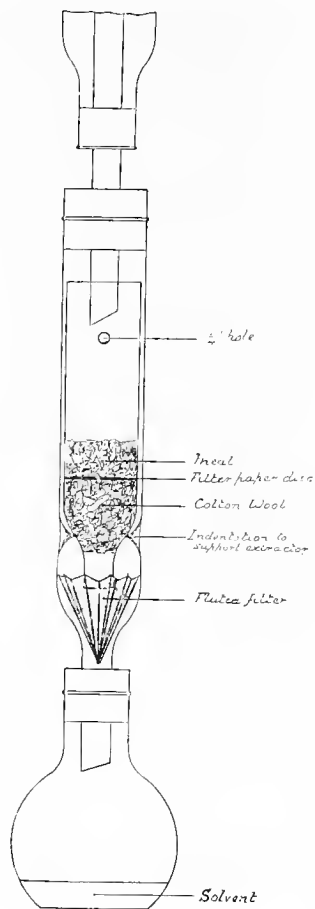
½″ hole

lineal
Filter paper disc
Cotton Wool
Indentation to
support extractor
Fluted filter

Solvent

Fig. 1.

The authors have devised a special form of extractor (Fig. 2) enabling the analyst to deal with varying quantities of material in the same apparatus and without undue loss of solvent. The details are easily seen from the sketch, three sizes of inner extraction tube being supplied with the apparatus. The general method of working it, is as described above.

As a general rule, from half to two hours is sufficient for the first extraction, after which the extractor is removed and the solvent allowed to spontaneously evaporate in a *moderately* warm place (too rapid heating may cause ejection of the contents). When the solvent has evaporated, the tube is placed in a water oven for about an hour, the contents having been first distributed over the walls of the tube by gentle tapping. After this the contents of the tube are transferred to a mortar, together with 1 or 2 grm. of clean dry sand (passing 60 mesh), and ground as finely as possible, the contents of the mortar being then carefully brushed back into the extractor, and the mortar washed out with the solvent. Extraction is then continued for an hour to an hour and a half, after which the flask is detached and the solvent distilled off with the flask in an inclined position (so as to prevent splashing of the fat on to the delivery tube), the flask being then placed in a water oven and dried to constant weight. The flask may with advantage be inclined side-

FIG. 2

ways, and turned from time to time. If heating be not unduly prolonged, there is little danger of appreciable increase of weight due to oxidation, and in the opinion of the authors the use of a vacuum drying apparatus is unnecessary, but on no account should a temperature of 105° C. be exceeded for drying.
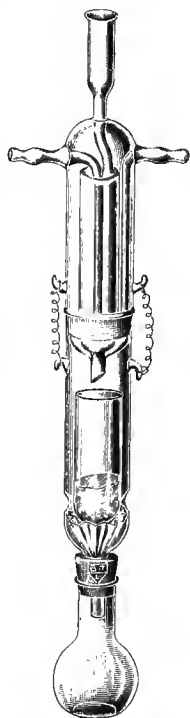
To obtain sufficient quantities of the fat for analytical examination an extractor of larger type may be employed, and the grinding with sand, as a rule, omitted.

PHYSICAL TESTS.

(a) Melting Point.

CAPILLARY METHOD.—The fat is melted and introduced into a tube about 0·025 in. bore, with the walls not more than 0·003 in. thick. The fat in the tube must then be thoroughly cooled, either by being kept on ice for half an hour, or allowed to stand at room temperature for at least twenty-four hours. Many fats may, however, be introduced into the tube by simply pressing it into the fatty mass, but in certain cases there is a danger of pressing out some of the softer constituents. If the latter method be resorted to, and the fat has been solid for twenty-four hours previously, it is obvious that no subsequent cooling is necessary.

The tube is attached to a thermometer by means of rubber bands and the thermometer clamped in position in a beaker containing not less than 500 c.c. of water, the top of the tube being submerged. The temperature of the water is now raised by means of a small flame, at the rate of about 0·5° C. per minute, the water being kept stirred by mechanical means, preferably by blowing a stream of air through the water. The fat is observed by means of a lens, and as soon as it is sufficiently melted to form a clearly defined meniscus on the top, the temperature is read and recorded as the point of *incipient fusion*. The heating is then continued until the fat is quite free from unmelted particles, the latter temperature being recorded as the point of *complete fusion*, which latter is usually returned as the *melting point*.

The difference between the points of incipient and complete fusion affords valuable information to the analyst as to the range of melting-point of the products of which the fat may be composed, and to the experienced eye may give a clue to the presence of high melting-point fats or waxes which may have been added.

(b) **Solidifying Point.**

Twenty-five to 30 c.c. of the melted fat are introduced into a tube about $1\frac{1}{2}$ in. wide and 5 in. long, in which is supported a thermometer by means of a cork. As soon as the fat shows any tendency to solidify stirring is commenced with the thermometer till the fat solidifies, the temperature being closely noted from time to time. In most cases after a steady fall the temperature will be seen to rise, the highest point then reached being the *solidifying point*. Many fats, however, do not show this rise very definitely, but gradually solidify without further fall of temperature, the mercury remaining stationary during the process. In such cases the stationary point may be taken as the solidifying point. The solidifying point of oils, liquid at the ordinary temperature of the air, is determined by immersing the tube in a freezing mixture.

With fats which give an indefinite solidifying point, it will be found that the solidifying point of the fatty acids may be obtained with much greater precision.

This determination is called :

THE TITER TEST.

For this test the preparation of the fatty acids must be carefully carried out, for on their purity the success of the test very largely depends. A simple and reliable method is as follows :

In a 300 c.c. flask are placed about 50 grm. of the fat, together with about 15 grm. of stick caustic soda,

and 100 c.c. of strong (95 per cent.) alcohol. The flask is connected to a reflux condenser, and heated in a boiling water bath with constant shaking until saponification is complete, which may be taken to be the case when the whole of the fat has gone into solution. The alcohol is then rapidly boiled off, and the soap dissolved in not less than 500 c.c. of hot water. To this solution, while still warm, are added one or two drops of methyl orange and somewhat more dilute hydrochloric acid (1 : 3) than is necessary to render the solution permanently pink, the solution being then kept in boiling water until the layer of fatty acids becomes quite clear. The water is syphoned off as completely as possible, and the residual fatty acids filtered through dry, soft, thick filter-paper, the operation being repeated until a perfectly bright clear filtrate results. The solidifying point of the fatty acids so obtained is determined in a similar manner to that of the fats themselves.

The above method is satisfactory for all ordinary purposes, but as in certain cases, especially in connection with soap manufacture, the necessary fats are bought and sold on a basis of the Titer test, it is necessary to carry out the final operation in a more standard manner.

The usual method is known as *Dalican's method*, and for this purpose the melted fatty acids, obtained as above described, are poured into the standard tube mentioned above ($1\frac{1}{2}$ in. $\times$ 5 in.) until it is half full. The tube is placed in a wide-mouthed bottle 10 cm. wide and 13 cm. high, and so fixed in the mouth that the whole of the fatty acids are inside the bottle. A carefully standardised thermometer (specially made for the purpose) is inserted into the fatty acids so that the bulb occupies a central position, and immediately

crystals form at the bottom of the tube the mass is stirred, with the thermometer, three times from right to left, and then three times in the contrary direction, and then continuously and rapidly with a circular motion, avoiding contact with the sides, care being taken to incorporate the solidified fatty acids as they separate, until the whole mass is uniformly turbid. The mercury is then carefully watched until it rises sharply, when the maximum temperature obtained is carefully noted. This point is the *Titer point*. Duplicate determinations should not vary by more than $0.1°$ C.

In determining solidifying points, it is of the greatest necessity that the fatty acids employed should be *perfectly dry*, otherwise erroneous results will certainly be obtained. Comparison of the solidifying point of the fat with its Titer point often affords very useful information as to the nature of the fat under examination.

	Melting point of fat or oil.	Titer test.	Difference.
Maize oil .	− 12	+ 18	30
Cotton oil	+ 3	+ 33	30
Soja oil .	− 6	+ 22	28˙
Sesamé oil	− 5	+ 24	29
Sunflower oil	− 18	+ 18	36
Linseed oil	− 16	+ 18	34
Hemp oil	− 20	+ 16	36
Poppyseed oil .	− 20	+ 16	36
Rape oil .	− 8	+ 13	21
Arachis oil	0	+ 27	27
Olive oil .	+ 5	+ 23	18
Castor oil	− 10	+ 3	13
Shea nut oil	+ 18	+ 52	34
Cocoa butter	+ 26	+ 49	23
Borneo tallow .	+ 28	+ 50	22
Coconut oil	+ 22	+ 23	1
Cohune oil	+ 20	+ 22	2

The above table will illustrate the relationship between the Titer of the fatty acids and the melting-

point of the fat or oil. The figures given are only rough averages, and it should not be forgotten that the figures for different specimens of the fats and oils are likely to vary sometimes considerably on either side of the figures in the table.

(c) **Specific Gravity.**

The specific gravity of all oils and fats may be determined most expeditiously and accurately in the ordinary specific gravity bottle, with a capillary bored stopper. A 25 grm. bottle is the most convenient, and its capacity at 15° C. should be determined, once and for all, with the greatest accuracy. The bottle is filled by pouring in the liquid fat or oil at a temperature slightly below that at which the determination is to be made, and is then immersed in water maintained at the desired temperature until all expansion has ceased; after which it is removed from the water, excess of fat or oil carefully removed, and the outside dried. The bottle is then weighed with the ordinary precautions.

As a general rule, the specific gravity of all fats and oils which are liquid at 15° C. are determined at that temperature; in all other cases the determination is made at the boiling point of water. For this purpose the bottle is immersed well over the shoulder in a beaker of water which is kept rapidly boiling, the bottle being conveniently kept in position by a wire holder. When expansion is complete, the surplus fat is removed with the finger, the flame turned out, and the bottle removed from the water after a short interval. It is wiped dry and allowed to attain the temperature of the air before being weighed.

When specific gravities at the boiling-point of water are to be compared with the specific gravity of water at 15° C. it is necessary to introduce a correction for

the expansion of the bottle. As the co-efficient of cubical expansion of glass is 0·000025, the correction for a difference of 85° (using a 25 grm. bottle) will be 0·0531, *which weight in grammes is to be added to the weight of water which the bottle contains at 15° C. before comparing it with the weight of fat obtained.* The greatest confusion has been introduced into the analysis of oils and fats by a senseless multiplicity of temperatures at which specific gravities are determined. The two temperatures of 15° and 100° (usually stated as 99°) are enough for all practical purposes.

For the routine examination of a large number of oils a Westphal balance may be employed, but the accuracy is not as great as that of the specific gravity bottle.

(d) Optical Activity.

In certain cases the examination of oils for optical activity is of some value, as the possession of this characteristic, in any marked degree, is limited to about half-a-dozen oils, most of which are either decidedly poisonous or possess marked physiological properties. The exhibition of optical activity must not be construed to be the result of the poisonous nature of the oil, as most essential oils, with which we are not here concerned, are optically active. If sufficiently clear, the oil itself is placed in the polarimeter tube, otherwise a chloroform solution is employed.

(e) Refractive Index.

This is most conveniently determined in the butyro-refractometer of Zeiss, which instrument reads on an arbitrary scale, the divisions of which are usually returned and are so given in this book, but which may be converted into true refractive indices $(n)_D$ by means of a table supplied with the instrument.

This value has been much complicated by the employ-ment of greatly divergent temperatures, often aimlessly selected. We propose to adhere to a uniform tempera-ture of 40° C. (at which practically all fats can be examined). In the case of one or two exceptions the reading is made at a higher temperature and calculated to 40° C. by adding 0.55 per $^{\circ}$C. above 40°, to the reading.

In the tables of figures for the various oils and fats in Chapters IV and V, the Zeiss butyro-refractometer number has been in all cases designated " refractive index at 40° C."

Construction and Mode of Action of Wollny's Butyro-Refractometer.

The refractometer consists of a heatable Abbe double prism and a permanently attached telescope, the objec-tive of which is adjustable in a slide by means of a micrometer screw. A scale, graduated from -5 to $+105$, is placed in the focal plane of the telescope objective ; the upper lens of the ocular is adjustable in order to be able to focus the lines and figures of the scale clearly.

Clear daylight is projected into the double prism by (j) and penetrates through the stratum of fluid between the prisms. The naturally coloured *border-line* of total reflection, produced by this passage of rays in the focal plane of the telescope, hence also in the plane of the scale, is *achromatised* in the case of butter by virtue of the special construction of the glass prism turned towards the telescope. Thus a *sharp colourless border-line*, which intersects the scale vertically, is seen in the ocular between a light and a dark section of the field of view. The accuracy of the measurement to be made then depends on the exact determination of the point in the scale through which the border-line passes.

ARRANGEMENT OF THE REFRACTOMETER AND OF THE HEATING
APPLIANCE.

The apparatus is withdrawn from its case by taking
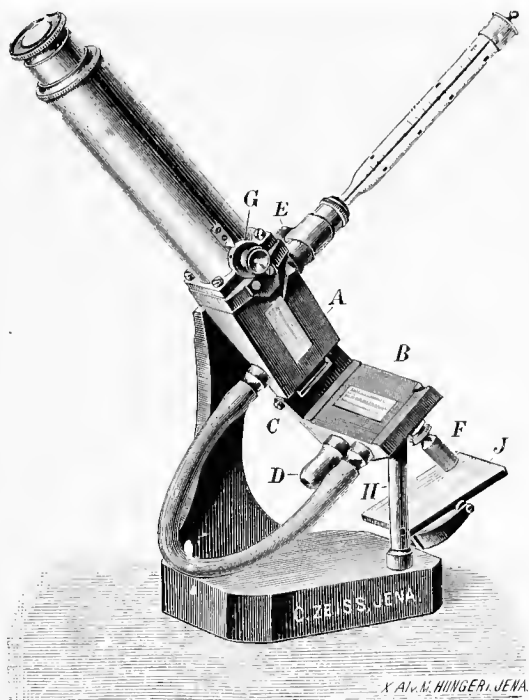
FIG. 3.

hold of the base plate or the telescope carrier—never
the telescope itself—and placed in a convenient position
for looking into the telescope.   The illumination may
be supplied either by the daylight coming in through a
window or by the light of a lamp.

The refractometer can be used in conjunction with

any kind of heating appliance which affords a current of water of constant temperature and uniform speed. Connection with the refractometer should always be established so that the water enters at (ʋ) and flows off at (ᴇ).

Application of the Sample to the Prisms.

The prism casing is opened out by revolving the screw head (ꜰ) (Fig. 3) clockwise, giving it a half turn until checked, when one half (ʙ) of the prism casing can simply be hinged down.   The surfaces of the prisms and of the metal parts must now be cleaned with scrupulous care, soft linen and a little alcohol or ether being best for the purpose.

A small quantity of the sample to be tested is then melted if necessary, and if not quite bright poured upon a small filter.   The first two or three drops of clear fat or oil percolating the filter are applied to the surface of the folding prism, in doing which it is expedient to tilt up the apparatus with the left hand, so as to bring the surface in question to an approximately horizontal position.   The observer now presses the component (ʙ) against (ᴀ) and turns the screw head (ꜰ) in the reverse direction to contact with another stop, whereby (ʙ) is secured against dropping back and close adhesion of the two prism faces is effected as well.   The apparatus is at the same time replaced on its base plate.   The mirror (ᴊ) should be arranged in such a position that the border-line appears distinctly, which may necessitate slight shifting or turning of the entire apparatus.   The draw at the ocular should also be adjusted so that the scale can be seen distinctly.

The first thing necessary is to ascertain that the entire space between the prism surfaces is uniformly

packed with fat.   For that purpose the small image of
the prism surface situated about 1 cm. in front of the
ocular is scanned with a magnifier held at the requisite
distance from the ocular (or with the naked eye).   In
this way minute air-bubbles within the stratum of fat,
which would prejudice the sharpness of the border-line,
will be readily detected.

If a current of water of constant temperature has
previously circulated for a time through the prism body,
the border-line will quickly—generally in about a minute
—assume a fixed position and attain the maximum
sharpness.   The position of the border-line relatively
to the scale is noted, and at the same time the tem-
perature registered by the thermometer is read off.

Integral divisions of the scale are read off immediately
in the field of view, tenths of a division being deter-
mined by the aid of the micrometer screw (G in Fig. 3)
in the following manner :   The border-line is adjusted
by means of the screw upon a division of the scale,
when the micrometer drum will indicate the number of
tenths to be added to the number of integral parts of
the scale appertaining to the particular division.

The use of sodium light illumination greatly sharpens
the border-line.

A standard fluid is provided for testing the adjust-
ment of the ocular scale and directions are given for
re-setting the scale when necessary.

CHEMICAL TESTS.

(a) Saponification Value.

Definition.—The saponification value is defined " as
the number of milligrammes of potassium hydroxide
which are required to completely saponify 1 grm. of the
substance."

When corrected for the *acid value* (see below) we obtain the *ester value* of the fat, which is in fact the *true* saponification value of the neutral glycerides present. From this ester value the following deductions may be made :

Since 56·1 grm. of KOH saponify one third of the molecular weight of the fat in grammes, it follows that the mean molecular weight of the fat under examination can be determined directly from the saponification value, and in a similar way the mean molecular weight of the fatty acids. It follows also that the ester value is a measure of the quantity of glycerine combined in the fat as glycerides, and the quantity of glycerine may be approximately arrived at by the following formula :

Ester value × 0·05466 = percentage of glycerine, as 1 grm. of KOH is equivalent to 0·5466 ᵗ grm. of glycerol.

Also the mean molecular weight of fat $= \dfrac{W \times 6000}{3\,y}$, where W = weight of fat taken, and y = c.c. of N/2 KOH for saponification, assuming the fat to consist of triglycerides.

The saponification equivalent is the number of grammes of fat saponified by 56·1 (*i.e.* one equivalent) of potassium hydroxide. It is obvious that this is merely another mode of expressing the same result, and the one figure can easily be calculated from the other. Köttstorfer's original mode of expression (saponification value) is now more generally used.

Method of carrying out the test.—Solutions required—

(1) N/2 hydrochloric acid, accurately prepared.

(2) Alcoholic potassium hydroxide, approximately N/2 strength.

(3) One per cent. alcoholic solution of phenolphthalein.

The potassium hydroxide solution is prepared by dissolving 17 to 20 grm. of stick potassium hydroxide (purified by alcohol) in the smallest possible quantity of water, and then making up to 500 c.c. with alcohol of not less than 94 per cent. (by weight). The solution is allowed to stand overnight, and the clear liquid syphoned off for use. If the alcohol be pure the solution will be colourless, or nearly so (it is advisable to test the alcohol before making up the solution, and to reject any which gives more than a very pale colour when boiled with a strong solution of sodium hydroxide).

The test is carried out as follows : About 2 grm. of the clear filtered fat are weighed into a 200 c.c. Jena flask, and an accurately measured quantity of the alcoholic potassium hydroxide solution run in from a 25 c.c. pipette. A like quantity of the same solution is run from the same pipette, in exactly the same way, into a clean 200 c.c. flask. The flasks are connected to reflux condensers and heated in a water-bath so that the alcohol boils gently for thirty minutes. The flask containing the fat should be shaken occasionally, particularly at the commencement. The flasks are then removed from the bath, 20 drops of phenolphthalein solution added to each, and the contents titrated while hot with N/2 acid.

If F = grm. of fat taken,

X = c.c. of acid required in the control experiment,

Y = c.c. of acid required to neutralise the excess of alkali in the test,

then the *saponification value* $S = \dfrac{(X-Y) \times 0{\cdot}02805 \times 1000}{F}$,

and the *saponification equivalent* $= \dfrac{56100}{S}$.

Precautions.—Great care should be taken with the solutions and during the test to avoid absorption of

carbon dioxide. A blank titration should be made
with every set of tests. The end point of the titration
should be ascertained *as exactly as possible*.

(*b*) **Iodine Value.**

The iodine value is defined as " the percentage of
iodine absorbed by an oil, fat or wax." It is in fact
a measure of the unsaturated bonds present in the
substance under examination, and is often taken to be
entirely due to the presence of *olein*, but while this is
true for a number of fats, there are many which contain
other unsaturated glycerides, such as occur in linseed,
arachis, cotton oil, etc., in which other more unsaturated
glycerides are present. The same applies to the *bromine
value*, so that one may be calculated from the other.

Several methods are employed for determining this
value, and though by far the greater number of figures
published have been determined by the Hübl method,
the authors now entirely employ the method of Wijs,
which is not only much easier of application, but more
rapid and reliable, and moreover the necessary reagent
is stable. Like most good methods it has suffered from
modification, but the original method is perfectly satis-
factory.

To carry out the test the following solutions are
required :

(1) *Decinormal sodium thiosulphate.*—Twenty-five
grm. of the pure salt are dissolved in water, and made
up to 1000 c.c. The solution, which will be found to
be of almost the right strength, may be standardised
against potassium bichromate solution in the following
manner : 3·863 grm. of pure potassium bichromate
(free from the sodium salt) are dissolved in water, and
made up to 1000 c.c. Each c.c. of this solution will
liberate 0·01 grm. of iodine (A.W. 126·92).

To standardise the thiosulphate solution 10 c.c. of a 10 per cent. solution of potassium iodide are placed in a flask together with 50 c.c. of water and 5 c.c. of concentrated HCl ; 20 c.c. of the bichromate solution are accurately measured in, and the solution titrated with the thiosulphate using a solution of soluble starch as indicator. The final green tint of the solution must not be mistaken for persistence of the starch iodide colour. Since the 20 c.c. of bichromate solution will have liberated exactly 0·2 grm. of iodine, the value of the thiosulphate solution in terms of iodine can be calculated.

It may be noted that the solution of bichromate keeps indefinitely.

(2) *Wijs' solution of iodine monochloride.*—Thirteen grm. of iodine are dissolved in a litre of acetic acid (Kahlbaum, 99 per cent.) by warming on the water-bath, protecting the solution from access of moisture. The solution is cooled, and about 100 c.c. poured into another vessel. Dry chlorine gas is passed into the remainder (which is kept in gentle motion), until the deep brown colour of the solution changes to a clear dark orange, when the passage of the gas is stopped. The iodine solution which was kept back is now added until the colour of the solution on mixing again becomes faintly brown. In this way a slight excess of iodine over that necessary to produce iodine monochloride is caused to be present in the solution, and so any danger of the presence of iodine trichloride avoided. This solution is quite stable under ordinary conditions, and will not alter in titre during some months, its keeping powers being still further enhanced by heating the solution in a water bath for fifteen minutes.

Dry chlorine gas is most conveniently prepared from bleaching powder by the action of dilute sulphuric acid.

The gas production is easily controlled if the bleaching
powder be first made into cubes by mixing the dry
powder with twice its weight of plaster-of-Paris and
moistening with sufficient water to produce a paste,
which, after being allowed to set, is broken up.   A
sufficient number of these cubes are placed in a large
flask, fitted with a sulphuric acid " bubbler " to regulate
the pace of evolution of the gas.

In order to avoid the preparation of chlorine, iodine
trichloride is now prepared in 10-grm. tubes, and the
contents of one of these tubes may be dissolved in about
300 c.c. of acetic acid, and a solution of 12 grm. of iodine
in about 500 c.c. of the same acid poured in until
the colour of the iodine solution, on mixing, is seen to
be no longer absorbed by the trichloride.   A slight
excess of the iodine solution is then added as before,
and the whole made up to a litre with acetic acid, and
heated for fifteen minutes in the water bath.

(3) *Soluble starch solution.*—About 1 grm. is dissolved
in 100 c.c. of water by boiling, and the solution is then
cooled. This solution must be made up fresh each day,
unless preserved by the addition of a few drops of carbon
tetrachloride well shaken with the solution.   Ordinary
starch may be used, but is not so sensitive as the soluble
variety.

(4) *Carbon tetrachloride.*—The ordinary commercial
re-distilled product may be employed, but it should be
previously dried over $CaCl_2$.

Method of carrying out the test. — For ordinary
work 10 c.c. of the Wijs' solution is employed by us,
and as this is a constant quantity, and the iodine
absorption of fats varies, a suitable amount of the
material to be examined must be weighed out, so that
only about half the halogen content of the solution
is utilised.   If the iodine value of the substance be

not known, a preliminary trial should be made. The
necessary amount (which will be between 0·1 and 1·5
grm.) is accurately weighed out into a clean dry flask, of
about 200 c.c. capacity, 5 c.c. of carbon tetrachloride
added, and the fat brought into solution. Ten c.c. of
the Wijs' solution *accurately* measured, are run in, a
stopper inserted, and the whole shaken round and
allowed to stand for thirty minutes. Five c.c. of a 10
per cent. solution of potassium iodide are then added,
followed by 50 c.c. of· water, and the contents of the
flask titrated with the standard thiosulphate solution,
adding about 10 drops of the starch solution towards
the end of the titration, which is then continued till the
violet colour does not return on well mixing the contents
of the flask. No notice should be taken of any colour
which re-appears on standing for some time, this being
due to decomposition of the iodine compound of the fat
by light. A blank experiment is conducted in an
exactly similar manner, using all the materials with the
exception of the fat. From the figures so obtained, the
iodine value is calculated by the following formula :

$$\text{Iodine value} = \frac{(a-b) \times F \times 100}{W};$$

where—a = c.c. of thiosulphate used for blank.

b = c.c. of thiosulphate used for the test.

F = weight of iodine equivalent to 1 c.c. of
thiosulphate solution, as determined in
the bichromate standardisation. If the
thiosulphate is strictly $N/10$, this will
be 0·012692.

w = the weight of fat used.

Precautions.—The iodine solution must be most
accurately measured, and on account of the high co-effi-

cient of expansion of acetic acid, measurements must always be made at the same temperature. Titration should be carried to the nearest half drop. In the case of high iodine values, or where very great accuracy is required, the quantities given above should be increased. The presence of moisture or alcohol vapour must be carefully excluded during the experiment.

(c) **Acetyl Value.**

The acetyl value is defined as " the number of milligrammes of potassium hydroxide required to neutralise the acetic acid obtained when 1 grm. of an acetylated fat or oil is saponified."

Since many fats and oils contain glycerides possessing one or more hydroxyl groups not in combination with glycerine, it is possible to obtain a measure of their presence by replacing the hydrogen of these hydroxyl groups by the acetyl radical. At the same time any free alcohols such as glycerol, cholesterol, etc., will be included if present.

Method of carrying out the test.—The form here given is that devised by Lewkowitsch. Ten grm. or any convenient quantity of the material are boiled with about twice their weight of acetic anhydride for two hours under a reflux condenser. The solution is then poured into a beaker of about 1000 c.c. capacity and mixed with 500 to 600 c.c. of boiling water, which is kept boiling for thirty minutes, during which time a fine stream of carbon dioxide is passed in to prevent bumping. The boiling is then stopped and separation allowed to take place, the water is syphoned off, and the heating with water again repeated three times until all trace of acetic acid is removed, but too prolonged washing is to be avoided. The acetylated fat

is then filtered through dry filter-paper until free from water.

About 5 grm. of this acetylated fat are saponified in an exactly similar manner to that employed in carrying out the saponification value. The alcoholic potash used must be accurately measured. After saponification the alcohol is distilled off, and the soap dissolved in water. To the solution is added $N/2$ H_2SO_4 in quantity exactly equivalent to the alcoholic potash employed, and the mixture is then gently warmed till the fatty acids separate completely as an oily layer. The acids are filtered off, washed with boiling water until the washings are no longer acid, and the total filtrate titrated with $N/10$ KOH to phenolphthalein.

$$\text{Acetyl value} = \frac{\text{Number of c.c. } N/10 \text{ KOH} \times 5\cdot61.}{\text{Weight of acetylated fat taken.}}$$

It is recommended to use a slight excess, say $1\cdot5$ c.c. of the $N/2$ H_2SO_4 in order to cause the fatty acids to separate easily from the solution, and this amount must be allowed for in titrating the filtrate with $N/10$ alkali. The distilled water used in this process must be carefully freed from CO_2 by boiling.

True Acetyl Value.

In the case of fats containing soluble fatty acids a correction has to be introduced, as a proportion, or in some cases all, of these will be washed out of the layer of fatty acids together with the acetic acid. The correction is easily determined by treating 5 grm. of the unacetylated fat in an exactly similar manner, employing exactly the same amount of water for the final washing as is employed to wash out the acetic acid. The total volume to be titrated with $N/10$ alkali is to be the same in each case. The connection of this

determination with rancidity is discussed under that heading.

The following are a few values selected from those given by Lewkowitsch.

The figures are *true* acetyl values, that is to say they have been corrected for the presence of volatile and soluble acids as stated above.

Oil.				True acetyl value.
Castor	.	.	.	.	150·05
Japan wax .	.	.	.	27–31·2
Croton	.	.	.	.	19·82
Rape	.	.	.	.	14·7
Safflower	.	.	.	.	16·1
Cotton-seed	.	.	.	14·8–15·65
Maize	.	.	.	5·81
Coconut	.	.	.	0·9–12·3
Lard	.	.	.	.	2·6

(*d*) **Bellier's Test for Arachis Oil in Liquid Vegetable Oils.**

The test is used as a qualitative method of determining the presence of arachis oil in admixture with other liquid vegetable oils.

The following solutions are required :

(1) An alcoholic solution of potassium hydroxide, made by dissolving 4·25 grm. of potassium hydroxide (stick, pure by alcohol, contains about 87 per cent. of KOH) in 70 per cent. alcohol and made up to 50 c.c.

(2) A solution of acetic acid, of which 1·5 c.c. will neutralise exactly 5 c.c. of solution (1). About 14·5 c.c. of glacial acetic acid diluted to 50 c.c. will give about the correct strength.

Method of carrying out the test.—In a test-tube

(6 in. by 1 in.) are placed $\aleph$ grm. of the oil which is saponified by heating gently with 5 c.c. of solution (1), till quite clear, shaking well and avoiding evaporation of the alcohol ; for which reason the tube is best held with the fingers.   As soon as saponification is complete, 1·5 c.c. of the acetic acid are added and the tube cooled in water at 18° C. for *not less* than 30 minutes, with occasional shaking.   To the solution are then added 50 c.c. of 70 per cent. alcohol containing 1 c.c. of strong hydrochloric acid per 100 c.c.   The whole is mixed and placed in water at 18° C. for one hour.   If arachis oil be in the original sample a distinct precipitate is formed, even when 5 per cent. only is present, the volume of the precipitate increasing with increasing proportions.

Other liquid vegetable oils only give at the most an opalescence and usually remain quite clear.   As olive oil sometimes gives a definite precipitate at first, it is advisable to warm up the solution and again place in water at 18° C.   Under these circumstances olive oil does not re-precipitate, while if arachis oil be present, the precipitate forms as before.

The test is quite reliable for liquid vegetable oils, but breaks down if solid vegetable or animal fats be present. Coconut and palm kernel oils are exceptions among the solid vegetable fats.

(e) Separation and Determination of Liquid Fatty Acids.

(Lead-Salt-Ether Method).

On account of the much greater solubility of the lead-salts of the liquid fatty acids (which may be taken to be practically oleic, linolic, and linolenic acids), they

may be separated in an approximately quantitative
manner by the following method : 5 grm. of the sub-
stance are saponified by boiling in a 300 c.c. flask
with 2 grm. of solid caustic soda (the usual stick caustic
soda, pure by alcohol, contains 87 per cent. NaOH),
and 50 c.c. of strong alcohol under a reflux con-
denser until saponification is complete.　If preferred
2 c.c. of the usual caustic soda solution used for
the Reichert-Meissl process may be employed for
the saponification.　Saponification being effected, the
solution is made slightly acid to litmus paper with
acetic acid, and titrated with an alcoholic solution
of caustic soda till neutral to phenolphthalein.　The
alcohol is then distilled off and the soaps dissolved
in 100 c.c. of water.　To this solution are added
gradually and with constant shaking, 200 c c. of a
filtered 2·5 per cent. solution of normal lead acetate,
previously raised to the boil.　The flask, if not already
full, is filled completely with hot water, and put aside
to cool.　When the lead soaps have become hard and
cold, the liquid is decanted off through a filter, and any
of the lead-salts left in the filter returned to the flask.
The contents of the flask are washed two or three times
with boiling water.　Before pouring off the water the
mixture is carefully cooled each time by a rapid rotation
of the flask under a stream of cold water.　The flask is
finally turned upside down and held over the filter by
means of a clamp, till as much of the water as possible
has drained off.　Should there be any particles of lead
salts on the filter they should be carefully picked off and
returned to the flask.　Two hundred c.c. of ether are
now added and the flask closed and thoroughly shaken,
after which the contents are boiled under a reflux
condenser with repeated shaking for thirty minutes.
By this means the lead salts of the liquid fatty acids

are dissolved out, the termination of the process being indicated by the separation of the insoluble salts in a pulverulent condition. The contents of the flask are allowed to cool, avoiding undue exposure to the air, and filtered into a separating funnel, the filter being kept covered as much as possible with a watch-glass. The insoluble salts in the flask are brought on to the filter with three or four successive quantities of 30 c.c. of ether. To the solution of the lead-salts in the separating funnel are added 100 c.c. of water, and an excess of hydrochloric acid. The separating funnel is then securely stoppered and vigorously shaken until lead chloride ceases to settle out.

The aqueous liquid and the precipitated lead chloride are now run off, and the ether washed with successive *small* quantities of water until the wash water is free from hydrochloric acid. The water having been separated as completely as possible, a few small pieces of granulated calcium chloride are added to the ether and the whole well shaken and allowed to stand for thirty minutes. The ethereal solution is poured through the *mouth* of the funnel on to a small filter, placed in a weighed flask (taking care that none of the calcium chloride solution finds its way on to the filter), the separating funnel being carefully rinsed with a few c.c. of fresh ether, which are then poured on to the filter. The ethereal solution is then distilled off, and the residual fatty acids either dried in the water oven, or if preferred, by placing the flask in hot water and attaching to a vacuum pump, but the vacuum employed must not be more than twenty inches of mercury or collapse of the flask may ensue.

The liquid fatty acids being thus obtained, their iodine value may be determined.

It must be borne in mind that these liquid fatty acids

are susceptible to oxidation, and that all reasonable care should be taken with them to avoid such oxidation. When dealing with drying oils, such as may occur in foodstuffs (for instance linseed, rubber-seed, sunflower, and perhaps maize and rape oils), it will be necessary to distil off the final ethereal solution in a current of hydrogen or carbon dioxide.

The following formulæ and iodine values will be of use in resolving mixtures when the iodine value of a known weight of the fatty acids is estimated :

Per cent.

Oleic acid   . $C_{18}H_{34}O_2$ (M.W. $= 282$) Iodine value $= 90$

Linolic acid   . $C_{18}H_{32}O_2$ (M.W. $= 280$)   ,, $= 181$

Linolenic acid . $C_{18}H_{30}O_2$ (M.W. $= 278$)   ,, $\begin{cases} = 245 \\ \text{approx.} \end{cases}$

Ricinoleic acid . $C_{18}H_{34}O_3$ (M.W. $= 298$)   ,, $\begin{cases} = 85{\cdot}5 \\ \text{approx.} \end{cases}$

Two modifications of the lead-salt-ether method are applied to the detection of *arachis oil* and *rape oil* respectively. They are carried out as follows—

(1) RENARD'S TEST FOR ARACHIS OIL (with Archbutt's modifications).—Ten grm. of the oil are saponified by heating in a dish with 2 grm. of caustic soda and 100 c.c. of strong alcohol, keeping a funnel over the dish for the first fifteen minutes, after which the solution is allowed to boil down to about 20 c.c. The contents are then rinsed into a separator with hot water, and while hot, the soaps are decomposed with hydrochloric acid and the fatty acids extracted with ether (after well cooling the mixture), and the ether washed free of hydrochloric acid. The ether is then run into a flask and distilled off and the fatty acids dried in the water-oven. The fatty acids are then dissolved in 50 c.c. of 90 per cent. alcohol and cooled to between 38°–42° C., and while at this temperature, 5 c.c. of a 20 per cent. solution of lead

acetate are added. The mixture is then cooled to 15° C. and allowed to stand for thirty minutes, when the alcohol is carefully decanted off through a filter and the lead soaps washed once on the filter with ether. The filter is then pierced and the lead soaps washed back into the flask with ether and the whole well shaken. The ether is then poured off through a filter and the soaps after draining again washed back into the flask with ether (after piercing the filter as before) and shaken well and again filtered. This is repeated about three times more, and the soaps being then brought entirely on to the filter, they are washed with fresh ether till the washings only give a faint brown colour when shaken with sulphuretted hydrogen water. (This rather complicated washing is avoided by pouring the original alcoholic mixture, containing the lead soaps, into a large plaited filter (15 cm.), and after the alcohol has drained, placing this in a Soxhlet extractor and extracting with ether till no colour with H_2S water is given.) The soaps on the filter are washed, while still moist, into a separator with a jet of ether (if necessary followed by 20 c.c. of dilute hydrochloric acid and again with ether), and then decomposed by adding about 20–25 c.c. of hydrochloric acid (sp. gr. 1.10), and shaking well till lead chloride ceases to separate.

The lower layer is then run off and the ether washed with water till free from lead chloride. The ether is mixed with two or three pieces of granulated calcium chloride and allowed to stand for thirty minutes, after which the ether is poured into a flask and the separator washed out with a few c.c. of ether, taking care not to pour out any drops of water. The ether is then distilled off and the fatty acids dried in the water oven. They are then dissolved in 50 c.c. of 90 per cent. alcohol and the solution cooled till crystals separate.

The flask is then closed with a cork, fitted with a thermometer, the solution warmed till clear, and the temperature of crystallisation observed, when a very good idea of the amount of arachis oil in the original sample will be obtained, using for this purpose the following table of Tortelli and Ruggeri (except when solid vegetable or animal fats—with the exception of coconut products —are present, when the results are fallacious).

Temperature of crystallisation.	Arachis oil per cent.
35–38° C.	100
31–33° C.	60
28–30° C.	50
25–26° C.	40
22–24° C.	30
20·5–21·5° C.	20
18–20° C.	10
16–17° C.	5

The acids must then be further purified in order to obtain the melting-point.

For this purpose the liquid is allowed to stand for about one to three hours at the temperature of the room (15°–20° C.), and the crystals then filtered off on a small filter or preferably on a Gooch crucible, the mass being washed two or three times with 90 per cent. alcohol and then with 70 per cent. alcohol till the washings give no turbidity on dilution with water.

The crystals are then dissolved off the filter with hot ether, the ether evaporated and the residue dissolved in sufficient 90 per cent. alcohol and allowed to crystallise. The crystals are filtered off and again crystallised from 90 per cent. alcohol. A small portion is then placed on a fragment of porous plate, and when dry the melting-point is taken. The melting-point should be between 72° C. and 73·5° C., and the point of incipient fusion should not be below 71° C.

The method is made quantitative as follows :

The original solution of the acids, as obtained from their lead salts, in 50 c.c. of 90 per cent. alcohol, is allowed to stand at laboratory temperature (if possible not above 20° C.) for three hours. The crystals are then filtered off, collecting the filtrate in a measuring cylinder, washing out the flask on to the filter with this filtrate. The crystals are washed three times with 5–10 c.c. of fresh 90 per cent. alcohol, receiving the filtrate each time in a test-tube and pouring back over the crystals two to three times (in order to be sure that the alcohol is saturated with the acids), the alcohol used being at the room temperature. These filtrates are all poured finally into the measuring cylinder. The crystals are then well washed with 70 per cent. alcohol,[1] and dissolved out into a tared flask with hot ether, dried and weighed. Their purity must be confirmed by the melting-point. If below 71° C., the treatment must be repeated. The weight obtained must be corrected for the *quantity of* 90 *per cent. alcohol used* in washing, as the acids are distinctly soluble in this alcohol.

The following correction table is due to Tortelli and Ruggeri :

Weight of mixed acids obtained (grm.).	Correction (grm.) to be added per 100 c.c. of 90 per cent. alcohol used for crystallisation and washing at—		
	15°	17·5°	20°
0·05	+ 0·031	+ 0·040	+ 0·046
0·10	0·036	0·045	0·052
0·20	0·048	0·056	0·062
0·30	0 055	0·064	0·071
0·40	0·061	0·071	0·078
0·50	0·064	0·076	0·084
0·60	0·066	0·080	0·088
0·70	0·067	0·082	0·090
0·80	0·069	0·083	0·092
0·90	0 070	0·084	0·092
1·00	0·071	0·084	0·091
2·70	0·073	0·082	0·091

[1] These washings are thrown away.

Pure arachis oil usually gives about 4·8 per cent. of mixed arachidic and lignoceric acids by the above method, so that the quantity obtained multiplied by 21 is taken to give the percentage of arachis oil in the original sample.

As with Bellier's test, this method gives excellent results as long as vegetable liquid oils are being dealt with ; when solid vegetable or animal fats (with the exception of coconut products) are present, the quantitative value of the test fails, but by repeated re-crystallisations of the acids from 90 per cent. alcohol, it is possible to determine the presence of arachidic acid by melting-point determinations, if a fair proportion of arachis oil was present in the original mixture. Failure to obtain crystals melting at 71°C. must not under these circumstances be taken to exclude arachis oil.

(2) TORTELLI AND FORTINI'S MODIFICATION AS APPLIED TO THE DETECTION OF RAPE OIL IN MIXTURES.

In carrying out this test the following details must be adhered to *exactly*. Twenty grm. of the oil are saponified with 6 grm. of potash dissolved in 50 c.c. of 90 per cent. alcohol by heating under a reflux condenser. The liquid is then neutralised to phenolphthalein with 10 per cent. acetic acid, and the solution then slowly poured into a boiling mixture of 200 c.c. of 10 per cent. lead acetate and 100 c.c. of water, shaking vigorously during the addition. The mixture is then cooled under the tap, maintaining a rotary motion until the soaps begin to stick to the sides (if they do not stick at first, they will do so during the first washing). The water is poured off and the soaps washed three times with 200 c.c. of warm (60 to 70° C.) water, the water being then drained off and the last drops removed with filter-paper. To the dried soaps are added 80 c.c. of

methylated ether and the whole is well shaken for
several minutes till the mass is broken up, when it is
heated under a reflux condenser for thirty minutes,
shaking at intervals. The flask is then closed and
placed in water *at exactly* 15° *C. for one hour,* after which
the contents of the flask are poured on to a filter, the
funnel being placed in the mouth of a separator, and
the filter closely covered till all the ether possible has
filtered out. The filter and contents are dropped back
into the flask and the ether treatment (boiling and
cooling) repeated in exactly the same way, using 40 c.c.
of ether, and the mass filtered as before, again tightly
covering the filter and allowing to drain as completely
as possible. The flask is then washed out with a
further 40 c.c. of ether on to the filter, the contents of
which are well stirred up with the ether, which is then
allowed to drain off. The combined ethereal solutions
of the lead salts so obtained are then decomposed in the
separator by shaking twice with 150 c.c. of 10 per cent.
hydrochloric acid, after which the ether is washed with
two quantities of 100 c.c. of water, the ethereal solution
being then run out into a dry flask and allowed to
evaporate spontaneously or by the use of gentle warmth
in a current of hydrogen. The liquid fatty acids so
obtained are dissolved in 40 c.c. of strong alcohol (97
per cent.) and a saturated solution of sodium carbonate
added until the liquid is saturated (Na_2CO_3 separates).
The alcohol is then distilled off and the residue dried,
first in the water oven, distributing it as much as possible
over the sides of the flask, and finally in a vacuum
desiccator for at least forty-eight hours. The dry
sodium soaps are then boiled with 50 c.c. of *absolute*
alcohol and filtered in a hot funnel, the insoluble residue
being boiled with a further quantity of alcohol and the
treatment repeated till nearly the whole has been

dissolved.   The mixed alcoholic filtrates are freed from
alcohol by distillation and the sodium soaps dried as
completely as possible in a vacuum desiccator over
sulphuric acid.

According to Tortelli and Fortini the test is concluded
as follows :

0·5 grm. of the dry soaps are placed in a large test-
tube and dissolved by heating in 20 c.c. of absolute
alcohol.   A thermometer is then placed in the mixture,
which is allowed to cool and the turbidity temperature
noted.

The following table gives some results obtained by
them :

Oil.	Turbidity temperature.
Olive .	. $20-24^{\circ}$ C.
Rape . .	. $45-50^{\circ}$ C.
1 pt. Olive ⎱ 1 pt. Rape ⎰	. $35-40^{\circ}$ C.
8 pts. Olive ⎱ 2 pts. Rape ⎰	. $30-35^{\circ}$ C.
9 pts. Olive ⎱ 1 pt. Rape ⎰	. $30-34^{\circ}$ C.
Cotton . . .	. $14-16^{\circ}$ C.
Sesamé . . .	. $18-20^{\circ}$ C.
Arachis . . .	. $18-22^{\circ}$ C.

The authors find it more satisfactory to dissolve 0·75
grm. of the soaps in strong alcohol (97 to 98 per cent.)
and to leave the solution to stand at a temperature of
20° C.   Under these circumstances rape oil commences
to precipitate in a granular form in fifteen to thirty
minutes, and 5 to 10 per cent. of rape oil in admixture
with other fats produces a spongy gelatinous precipitate
within two hours, while in the absence of rape oil no
precipitate usually forms under fifteen to eighteen hours.

As the results are dependent on the degree of dryness of the soaps and the strength of the alcohol employed it is more satisfactory to carry through the test with some oil, such as cotton-seed oil, as a control. The test under these conditions is quite reliable.

(f) **Acid Value.**

The acid value of a fat or oil is a measure of the free fatty acidity, and is defined as " the number of milligrammes of potassium hydroxide required to neutralise the free fatty acids in one gramme of the fat or oil."

Method of carrying out the Test.—About 5 grm. of the fat or oil are weighed into a 250 c.c. flask, and 30 to 50 c.c. of 95 per cent. alcohol (which has been just previously boiled, and rendered faintly pink to phenolphthalein by the addition of N/10 NaOH) added. The mixture of fat and alcohol is brought to the boil (the oil does not usually dissolve, but the solution of the free fatty acids will have been effected) and titrated hot with N/10 NaOH till a faint pink colour, permanent on gently mixing the contents of the flask, is attained.

The acid value is calculated by the following formula :

$$\text{Acid value} = \frac{N \times 5\cdot61}{W},$$

where N = number of c.c. of N/10 NaOH used.

$\qquad W$ = weight of fat taken.

This formula gives the acid value in terms of the definition given above, but the acidity is for other purposes sometimes returned as " *per cent. of oleic acid*," in which case the above formula becomes—

$$\text{Oleic acid per cent.} = \frac{N \times 2.82}{W},$$

where 282 is the molecular weight of oleic acid.

In the case of coconut oil (particularly for soap making) it is now becoming the custom to return the acidity as *lauric acid,* as this figure represents very nearly the exact weight of the free fatty acids present. In this case the formula becomes :

$$\text{Lauric acid per cent.} = \frac{N \times 2.0}{W},$$

the molecular weight of lauric acid being taken as 200. Various other methods of calculation are also employed ; for example, on the continent the *Köttstorfer value* is often given, this being simply the number of c.c. of N. KOH required, using 100 grm. of fat.

The relationship of these methods of returning the acidity may be found from the following proportion :

Acid value.		Oleic acid.		Lauric acid.		Köttstorfer value.
1	:	0·5027	:	0·357	:	1·782

(*g*) **Hexabromide Test (Halphen's Modification).**

This test furnishes a method of distinguishing qualitatively between the fish, marine animal and drying oils on the one hand, and the non-drying oils on the other. It is useful for detecting the presence of the former in the latter.

Method of carrying out the test.—In a small dry test-tube are placed 0·5 c.c. of the oil and to this are added 10 c.c. of a mixture of twenty-eight parts by volume of glacial acetic acid, one part of bromine and four parts of nitrobenzene. The tube is then closed, the contents shaken and the behaviour of the liquid noted.

Such *non-drying* oils as *coconut products, olive, castor,*

arachis, cotton, sesamé, poppy-seed, etc., give *no precipitate* or only a *very slight turbidity,* even after standing for one hour. The *drying* oils, such as *linseed, rubber-seed, hemp-seed, etc.,* and *marine animal* and *fish oils,* such as *whale oil, japanese sardine oil,* etc., give a *precipitate* which settles more or less rapidly to the bottom of the tube, the precipitate from whale oil being much heavier than from fish oils and the drying oils. *Rape oil* is distinguished by forming a turbidity, and the liquid separates on standing into two distinct layers, but the mixture resolves into a clear homogeneous liquid on mixing with an equal volume of methylated ether.

As little as 5 per cent. of the drying and marine animal and fish oils can be detected by this means in admixture with such liquid vegetable oils as give no precipitate themselves.

When examining rape oil for these, the test should be mixed with 10 c.c. of methylated ether, as noted above, when, if only rape oil be present, the liquid will clear, but if the drying or marine animal oils be present, a precipitate will remain and slowly settle down.

Ten per cent. of rape oil in liquid vegetable oils can be detected by the production of an oily layer and the clearing of the mixture on the addition of ether.

It is usually stated that such animal fats as beef and lard give no precipitate, but the authors have found that beef and lard fats and also shea butter all give precipitates with this test.

Beef and lard fats give a flocculent precipitate which eventually rises to the top of the tube and is not dissolved by ether.

Butter fat as a rule behaves in a similar manner, but the precipitate is usually dissolved by ether.

Shea butter gives a precipitate which settles to the bottom of the tube and is insoluble in ether.

(*h*) **Phytosteryl Acetate Test and Unsaponifiable Matter.**

Animal and vegetable fats are both characterised by containing very small quantities of a complex alcohol. In the case of animal fats this is called *cholesterol*, $C_{27}H_{45}OH$, and apparently the same substance is found in all animal fats. Isomeric alcohols called *phytosterols* have been isolated from vegetable fats and oils, though apparently these are not always identical, yet very similar in properties. These two alcohols differ in their melting-points (cholesterol 147° C., phytosterol 137° C.) and differ somewhat in their method of crystallisation from alcohol, but are most easily distinguished by means of their acetates, which can be easily prepared, and, on account of their difficult solubility in 95 per cent. alcohol, purified by recrystallisation.

The melting-points of these acetates are sufficiently far apart to detect admixture of one with the other, and on account of the greater solubility of cholesteryl acetate in 95 per cent. alcohol the presence of small quantities of phytosteryl acetate can be detected in the presence of the other by the steady rise of the melting-point on repeated crystallisation of the mixture. This property provides a delicate method of detecting the presence of vegetable fats in animal fats when no other evidence is forthcoming.

The acetates are readily prepared from the sample by the following method :

Fifty grm. of the filtered fat are boiled with 75 c.c. of 95 per cent. alcohol under a reflux condenser. The flask is then cooled, the alcohol poured off into a weighed flask, and the fat again boiled up with another 75 c.c. of alcohol, after which the flask is cooled and the alcohol again poured off. The alcoholic extract of

the fat so obtained will contain practically the whole of the unsaponifiable matter, and some fat. The alcohol is distilled off, and the flask re-weighed in order to get a rough idea of the weight of the fat present. To every 5 grm. of fat are added 2 grm. of NaOH and 50 c.c. of alcohol and the mass saponified. The flask is then washed out into a porcelain basin, and the whole evaporated, stirring occasionally. When practically all the alcohol has been evaporated, twice as much sodium bicarbonate as NaOH used are added and a couple of small spoonfuls of fine sand, and the mixture well stirred and carried to dryness. The dry residue is thoroughly ground, dried in the water oven, and then extracted for three to four hours in a flow-through extractor with petroleum ether *free from residue*, and the unsaponifiable matter obtained by distilling off the ether. The *nature* of the unsaponifiable matter may be roughly ascertained by its behaviour on treatment with acetic anhydride. For this purpose the residue from the ether is dissolved in the smallest possible quantity of hot absolute alcohol, and washed into a small (1 oz.) well-stoppered bottle, the flask being rinsed out once or twice with small quantities of hot absolute alcohol. The alcohol is evaporated off, and to the residue left in the bottle are added 2 to 3 c.c. of pure acetic anhydride. The stopper is then carefully tied in and the bottle heated in boiling water for fifteen to thirty minutes. During this process the behaviour of the solution is carefully noted. If after fifteen minutes' heating the solution, when cool, remains clear, the presence of anything but traces of hydrocarbons is negatived, but if the solution shows the presence of an oily layer, it may be taken as almost certain that paraffin wax or some mineral oil is present in the original substance. In this case it will be necessary to

estimate the amount of these substances by the method
given below.   If, however, the acetic anhydride solution
be clear, the bottle is heated for a further ten to fifteen
minutes.   The stopper is then carefully removed and
the anhydride allowed to distil by heating in an oil
bath at 140°–150° C.   The contents of the bottle are
dissolved in a few c.c. of absolute alcohol, and if
the solution be coloured, mixed with about 1 grm. of
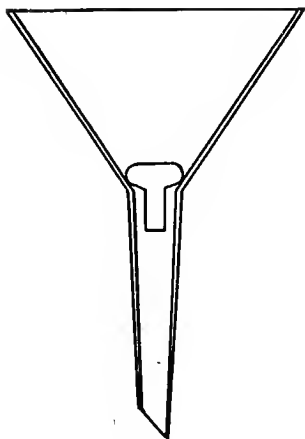
Fig. 4.

very finely ground recently
ignited animal charcoal,
the stopper again inserted
and the bottle heated in
boiling water with repeated
shaking until the liquid
is   seen   to   be   nearly
decolourised.   The con-
tents of the bottle are
then filtered into a small
beaker, rinsing the char-
coal and filter two or
three   times   with   small
quantities of boiling
absolute alcohol. (In those
cases in which the first
alcoholic solution of the
acetate is practically colourless, the above procedure is
unnecessary.)   The contents of the beaker are evapor-
ated to dryness, the residue dissolved in the least
possible quantity of hot 95 per cent. alcohol, and the
solution allowed to crystallise.   The liquid is poured off
into the small funnel shown in the illustration, protect-
ing it from evaporation by a watch-glass, and the
crystals washed with a few drops of cold 95 per cent.
alcohol, which is then poured over the crystals in the
funnel.   The contents of the funnel are washed back

into the beaker with a few drops of hot 95 per cent. alcohol, and the crystals dissolved by heating, and the solution again allowed to crystallise. The liquid is filtered off as before, and a few of the crystals spread on a porous plate and their melting-point determined. The contents of the beaker and funnel are washed again with a few drops of 95 per cent. alcohol and the recrystallisation and washings repeated three times more, a few crystals being removed each time, dried on porous porcelain, and the melting-point taken. If the melting-points of the fourth and fifth crystallisations are approximately the same, no further crystallisation will be necessary. If the melting-point be below 116° C. (corrected)[1] the presence of phytosterol may be negatived,[2] but if the melting-point lies higher than this, and tends to rise somewhat on further crystallisation, phytosterol may be assumed to be present with certainty. Should the temperature be 120° C. (corrected) or above there will be no doubt as to the presence of phytosterol. The melting-point of cholesteryl acetate is 113° C. (corrected), and of phytosteryl acetate 125°–133° C., dependent on the kind of vegetable fat used. The above process requires some care in carrying out, but if the above directions are *carefully* followed, no difficulty will be experienced.

In those cases in which observation of the acetic anhydride solution has shown the presence of hydrocarbons, or wax, the percentage of these may be ascertained with sufficient accuracy in most cases by determining the unsaponifiable matter in the following manner :

[1] *Stem Correction for Thermometer.*

$$T^1 = T + n \ (T-t) \ a \ ;$$

where T = indicated temperature,
 t = room temperature,
 n = number of degrees exposed at $t°$,
 T^1 = true temperature of bath,
 a = co-efficient of expansion of mercury in glass (0·000154.)

[2] See pp. 48–49.

Determination of Unsaponifiable Matter.

Five grm. of the fat are weighed into a large porcelain basin and heated with sufficient strong aqueous solution of caustic soda to introduce 2 grm. of NaOH and 100 c.c. of strong (95 per cent.) alcohol, the dish being covered with an inverted funnel. The dish is heated on a boiling water bath with occasional stirring for thirty minutes, after which the contents are evaporated to a pasty condition, when a teaspoonful of sand and 2 to 3 grm. of sodium bicarbonate are added and the whole carefully mixed and carried to dryness. The contents of the dish are then well ground, thoroughly dried and carefully transferred to a flow-through extractor, and extracted for two to three hours with petroleum ether. The contents of the extractor are dried, removed to a mortar, again thoroughly ground, dried in the water bath and extracted as before for another hour. The contents of the flask are then evaporated, dried and weighed as *unsaponifiable matter*, the percentage, when anything more than traces of wax or hydrocarbons are present, being taken to consist of those substances.

As small quantities (less than 0·01 per cent.) of paraffin wax are sometimes added to lard in order to defeat the detection of vegetable oils by the phytosteryl acetate test, it is necessary to treat the unsaponifiable matter in such cases by a method due to Polenske in order to circumvent this form of sophistication. This method has been very carefully investigated by Lewkowitsch. He points out that if the paraffin wax be as much as 10 per cent. of the unsaponifiable matter, a minute drop of paraffin wax will be seen floating on top of the acetic anhydride during acetylation, and the acetylated mass on successive crystallisations will show an abnormal and

probably decreasing melting-point.   In a case cited by
him, the melting-point of the second crystallisation of a
mixture of 90 per cent. cholesterol and 10 per cent.
paraffin wax was 90° to 99° C., and of the fourth crys-
tallisation 86° to 92° C.   A mixture, however, of choles-
terol, with small quantities of phytosterol together with
about 7 per cent. of their weight of paraffin wax, gives
melting-points for the acetates which can scarcely be dis-
tinguished from that of pure cholesteryl acetate. If, there-
fore, such small quantities of paraffin wax are suspected,
the unsaponifiable matter from at least 100 grm. of fat
should be prepared as above described, and decolourised
by dissolving in absolute alcohol, and heating under a
reflux condenser with a small quantity of finely ground
and recently ignited animal charcoal, filtering and
washing the charcoal with a very little absolute alcohol,
the clear filtrate being then evaporated to dryness.
The unsaponifiable matter so obtained from 100 grm.
of fat is shaken with 1 c.c. of light petroleum ether for
twenty minutes at 15° to 16° C.   The mixture is then
poured into a small funnel plugged with a small piece of
glass wool, and the undissolved matter in the funnel
washed five times with 0·5 c.c. of the ether.   The
residue on the filter is then acetylated as described
above, and the melting-point taken after the necessary
recrystallisations.   To determine the amount of wax the
ethereal filtrate is evaporated to dryness and heated with
5 c.c. of pure concentrated sulphuric acid at 105° C. for
at least an hour.   The wax is then extracted by shaking
the diluted acid with petroleum ether and weighed.

According to Polenske it is preferable to repeat the
treatment with sulphuric acid if the amount of paraffin
wax is very small.   The method, in spite of the apparent
complications, is capable of great accuracy if due care
be exercised in carrying out the various details.

Lewkowitsch has also shown that further valuable information may be obtained by acetylating the unsaponifiable matter in the usual way, and saponifying the weighed mixture of acetates and paraffin wax with alcoholic potash, so as to obtain their saponification value. The saponification value of cholesteryl acetate being taken as 135·5, the amount of paraffin wax in the mixture which was saponified may be calculated by the deviation from this value, and the process allows of both the cholesterol and the paraffin wax being recovered and dealt with, if desired, by Polenske's method as given above.

THE SEPARATION OF CHOLESTEROL AND PHYTOSTEROL.

While the above process of recrystallising the mixed acetates is in nearly all cases sufficient to demonstrate the presence of even small quantities of phytosterol in admixture with cholesterol, the reverse is not true, and the necessity may arise when lard or beef fat is suspected in hard vegetable fats.

In order to demonstrate the presence of a small quantity of cholesterol in admixture with phytosterol it is necessary to resort to a rather complicated process of separation, which is not likely to be successful unless the unsaponifiable matter is obtained from nearly 1000 grm. of the substance.

The sample is treated as described above (p. 48), preferably in lots of 200 grm., and the alcoholic extracts united. The final dry mixture of soaps, sand and unsaponifiable matter is extracted most simply by heating it in a flask under a reflux condenser with sufficient petroleum ether to rather more than cover the solid matter. After boiling gently for one hour the ether is filtered off and the solid matter dried and re-ground and boiled twice

more with petroleum ether. The combined ethereal extracts are then distilled to obtain the unsaponifiable matter. This is carefully shaken with a very small quantity of petroleum ether, increasing the amount until about one quarter of the total remains undissolved (cholesterol is more soluble than phytosterol). The ether solution is filtered and distilled off, and the residue is treated by the method of Windaus (Chem. Zeit., 1906, xxx, p. 1011). To each gramme of the residue are added 10 c.c. of dry methylated ether and solution effected. To the solution are added 10 c.c. of a solution of 5 grm. of bromine (dry) in 100 c.c. of *glacial* acetic acid and the mixture cooled in ice for an hour. If only small quantities of cholesterol are present the dibromide will not separate, in which case 50 per cent. acetic acid is added until a permanent turbidity appears. A further 2 to 3 c.c. of the 50 per cent. acetic acid are then added, and after a short time the precipitate filtered off on a very small hard filter and washed with a few drops of the 50 per cent. acetic acid. The filter-paper and contents are dropped into a small flask, 5 c.c. of glacial acetic acid and about 0·25 to 0·5 grm. of zinc dust added, and the whole boiled under a reflux condenser for two hours. The contents of the flask are then washed into a *small* separator with 20 c.c. of water and finally with 10–20 c.c. of methylated ether and the whole shaken. The aqueous layer is run off and the ether washed three times with a little water and filtered (if necessary) into a test-tube and the ether boiled off. The residue is dried in the water oven and then washed out with a very small quantity of absolute alcohol into a small evaporating basin and evaporated to dryness. The residue is covered with 1–2 c.c. of acetic anhydride, and the basin closed with a clock glass and heated on a water bath for thirty minutes. The acetic anhydride is

then distilled off, and the residue, if much coloured, washed with absolute alcohol into a test-tube and boiled with a little recently ignited powdered animal charcoal. The mixture is filtered (washing the charcoal with a little absolute alcohol) into a small beaker, evaporated to dryness and recrystallised from the least possible quantity of 95 per cent. alcohol ; the crystals are separated, recrystallised from 95 per cent. alcohol, and the melting-point taken, and further recrystallisations carried out if possible. The crystals, if cholesteryl acetate, should melt below 116° C. Twenty per cent. of cholesterol in the presence of phytosterol can be found by this means, and probably 10 per cent. may be found with care when a large quantity of material is employed to start with.

Colour Tests for Oils.

Of the many colour tests which have been described for the detection of certain oils the following are alone of any importance.

HALPHEN'S TEST FOR COTTON-SEED OIL AND COTTON-SEED " STEARINE."

The test is carried out as follows :

2·5 c.c. of the liquefied sample are dissolved in an equal quantity of amyl alcohol in a strong test-tube, and 2·5 c.c. of a 1 per cent. solution of sulphur in carbon disulphide added. The tube is then securely corked with a sound cork, which is well tied down with a piece of linen. The tube and its contents are placed in a boiling water bath for exactly thirty minutes. In the presence of cotton-seed oil or cotton-seed " stearine " a characteristic *crimson colour* is produced, and in this way as little as 1 per cent. of these oils may be detected. An approximate idea of the *amount* of cotton-seed oil

present may be obtained by comparing the colour developed, with that of standard tubes of mixtures containing known quantities of cotton-seed oil which have been treated in an exactly similar manner. The gradation of the colour is distinct up to 20 per cent. of cotton-seed oil, and if this limit be reached in the test the original sample should be diluted with some indifferent oil in order to bring the colour shade within the desired limits. It is quite satisfactory to keep a series of standard tubes for comparison, but under these circumstances the comparison should not be made until after twenty-four hours' standing, and both test and standard should be warmed to such a temperature that the contents are entirely fluid.

It should be noted that all specimens of cotton-seed oil do not give the same intensity of colour, and some oils which have been highly refined by certain modern processes produce very much less colour than the original oil. For this reason the quantitative indication of this test must be accepted with reserve.

If an indefinite reaction be obtained, the test may often be rendered more certain by applying it to the fatty acids. It must be remembered that *kapok* oil is the only known oil that gives a colouration with this test similar to that given by cotton-seed oil.

In order to distinguish these two oils recourse must be had to Becchi's test as modified by Millau (p. 54).

Baudouin's Test for Sesamé Oil.

The test is carried out as follows: Ten c.c of the melted fat are placed in a test-tube and two drops of a 2 per cent. alcoholic solution of furfural added, together with 10 c.c. of concentrated hydrochloric acid. The tube is then well shaken, when in the presence of sesamé oil *a crimson*

colour will be developed. The test is generally sensitive to 1 per cent. of sesamé oil. It must not be forgotten that many of the artificial colouring matters used in butter and margarine give a similar colour when shaken with hydrochloric acid. It is necessary, therefore, when examining these fats for sesamé oil to carry out a blank test, only omitting the furfural, any preponderance of colour in the test being attributed to sesamé oil.

The alcoholic solution of furfural keeps indefinitely in the dark. If furfural be not available, the oil should be shaken with 10 c.c. of concentrated hydrochloric acid which has been saturated, by shaking in the cold, with finely powdered cane-sugar.

The above reaction is not given by any other known oil, and for this reason sesamé oil has been made an obligatory ingredient of margarines intended for use in most Continental countries.

Becchi's Test.

This well-known test has been superseded by Halphen's test for cotton-seed oil. The modification of the test devised by Millau is, however, of use to distinguish kapok oil from cotton-seed oil when applied in the form recommended by Durand and Baud.

The test is carried out as follows:

Fifteen c.c. of the oil are saponified with caustic soda and alcohol in the usual manner, 200 c.c. of boiling water are added and the whole boiled till the alcohol is evaporated. The fatty acids are then thrown out by the addition of $N/10$ H_2SO_4 in slight excess. The fatty acids are skimmed off, and shaken twice with 15 c.c. of *cold* distilled water, the water being then drained off and the fatty acids dried rapidly in an oven at $105°$ C. Five c.c. of these fatty acids are shaken with 5 c.c. of a 1 per cent. solution of silver nitrate in absolute alcohol.

Under these circumstances cotton-seed oil only produces a *barely perceptible brown colour*, while kapok oil rapidly develops a *deep coffee coloration*. By means of this test it is possible to recognise 1 per cent. of kapok oil in other liquid oils.

Rosin.

This substance ought not to appear in edible products, but as occasion may arise which may necessitate its detection and estimation, the methods are here described.

(a) *Liebermann-Storch Reaction.*

A few drops of the sample are boiled with 2 or 3 c.c. of acetic anhydride in a porcelain basin, and the undissolved fat separated by filtration after cooling. The filtrate is placed in a porcelain basin, and sulphuric acid (sp. gr. 1·53) is allowed to drop gently on to the surface of the liquid. If rosin be present a characteristic *violet* colour is produced, which fades to a brown. This test will detect very minute amounts of rosin, but it should be borne in mind that cholesterol gives a similar colouration, though, in general, the small amount of the latter present in fats will not be sufficient to vitiate the test.

(b) *Quantitative Determination of Rosin by Twitchell's Process.*

This process will be found to give the most reliable results. About 2 grm. of the sample are dissolved in 25–30 c.c. of *absolute alcohol* and *dry* hydrochloric acid gas is passed into the solution, which should be kept cooled in water. After the gas has been passed for about an hour, the completion of the operation will be

shown by the escape of unabsorbed gas from the liquid.
The gas is then stopped and the flask is allowed to stand
for another hour.   About 150 c.c. of water are now
added, together with a piece of pumice, and the whole
boiled till quite clear.   The contents of the flask are
cooled, and the oily layer, consisting of neutral fat,
ethylic esters, and the rosin acids, is dissolved by
vigorously shaking with ether in a separator, the flask
being carefully washed out several times with ether.
The ether is allowed to separate, the aqueous layer
drawn off and the ether washed with successive portions
of distilled water until free from hydrochloric acid.   A
volume of alcohol equal to that of the ether is poured
into the separator, and the contents titrated therein
with N/2 KOH to phenolphthalein.

Then :

$$\text{Rosin per cent.} = \frac{\text{c.c. of N/2 KOH} \times 34\cdot6.}{\text{Weight of the substance} \times 2.}$$

This formula assumes 346 as the combining equivalent
of rosin, which of course is not necessarily true for all
forms of rosin, but the results obtained by the above
method are sufficiently accurate for the practical
purposes of this book.

In cases where free fatty acids are present and the
acid value has to be determined, the rosin acids will
be titrated together with the free fatty acids in the
usual determination of the acid value.   The total acid
value must therefore be corrected for the quantity of
rosin acids found, if the true acid value of the fatty
acid be required.

Microscopical Examination for Beef and Lard Fats.

If either of these fats be suspected, but no idea has
been obtained as to the amount present in a sample,

KEY TO PLATE I.

1
Beef fat
(polarised light).
× 150.

2
Beet fat
polarised light).
× 70.

3
Beef fat.
× 150.

4
Lard.
× 250.

5
Lard.
× 150.

PLATE I.
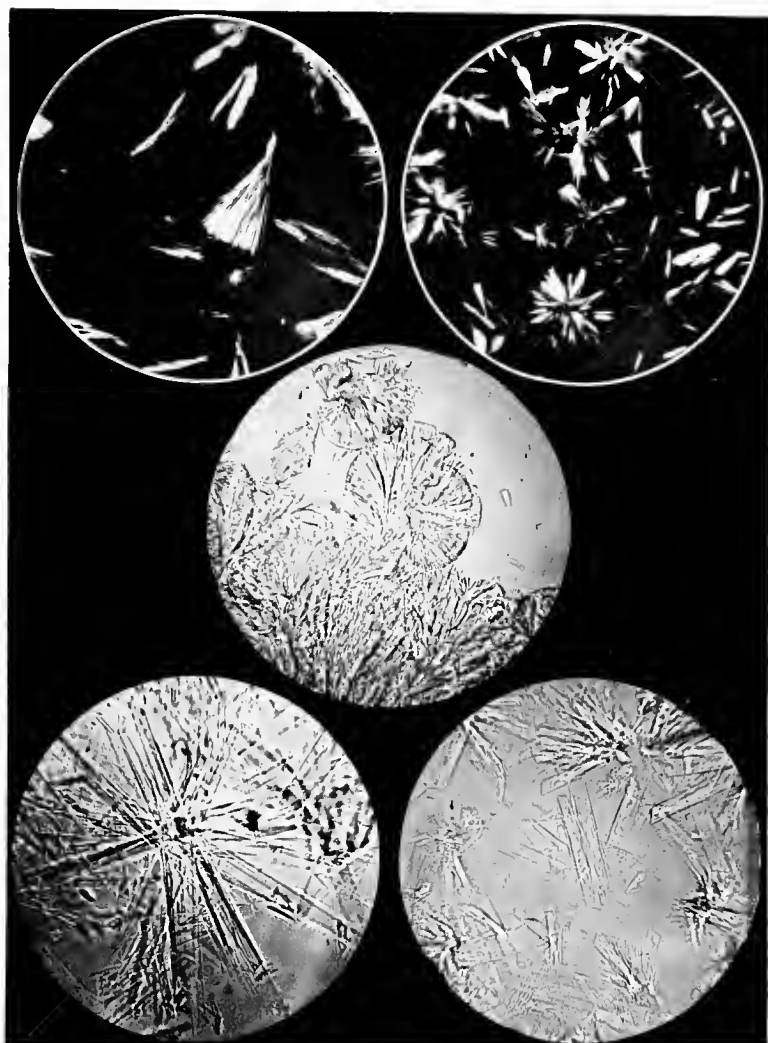
BEEF AND LARD CRYSTALS.

two separate mixtures of 2 and 5 grm. of the fat respectively with 10 c.c. of methylated ether (sp. gr. 0·720) are made in test-tubes, which are then closed with cotton-wool and allowed to stand at a temperature of about (but not below) 20° C. for twenty-four hours, or less if much crystallisation occurs before the lapse of that time. A piece of glass tubing, closed at one end with the finger, is lowered into the mixture till it touches the crystalline mass, when, on removing the finger, some of the crystals will pass into the tube, and may be removed from the liquid. A very small portion is dropped into the centre of a drop of clove oil previously placed on a microscope slide, and quickly covered with a cover-glass. The crystals are then examined with a $\frac{1}{2}$-in. and finally with a $\frac{1}{6}$-in. objective. Beef fat crystallises in characteristic *fan-like tufts*, the ends of which are more or less pointed, but are *never chisel-shaped*, as in the case of lard. The examination of the ends should be carried out with the higher power. The examination must be carried out with great care, as it often happens that lard crystallises in bunches of plates, almost identical with the fan-like tufts of beef-fat, but the ends of the crystals will be found to be distinctly chisel-shaped, while those of beef are pointed or round. If, however, lard crystals are recrystallised several times, the characteristic chisel-end formation may be lost and the crystals become indistinguishable from those of beef. Inferences, therefore, as to the presence of lard should only be drawn from the results of the *first* crystallisation. The appearance of the crystals is shown in the plate given. The authors find it very convenient to carry out the examination on the crystals deposited from the Halphen tube after boiling in the water bath as described on p. 52. For this purpose the tubes

are stood aside at room temperature until crystals deposit. A rough idea is then obtained of the amount of beef fat present by comparing the volume of the deposit with that from standards made up in a similar way with known amounts of beef fat. The supernatant liquid is poured off from the crystals and these are dissolved by the addition of 10 c.c. of methylated ether, warming till solution takes place, the tubes being then plugged with cotton-wool, and allowed to stand at room temperature to crystallise, and the crystals examined as described above. If no crystals deposit on standing for twelve hours, it should not be inferred that beef fat is absent *until the tubes have been cooled to 0° C. for not less than thirty minutes*. Under these circumstances very small quantities of beef fat will deposit, *but the presence of beef fat must be established microscopically*. (See p. 134.)

This method gives very characteristic crystals. It is well to note in this connection that shea nut oil deposits crystals which, though not identical with, are sufficiently like those of beef fat to be mistaken for them. Usually if there is sufficient of this oil to give crystals, some indication of its presence will be arrived at from the somewhat high amount of unsaponifiable matter present in the sample. (See shea nut oil.)

Björklund's Test.

(As interpreted by Lewkowitsch for the examination of cocoa-butter).

Three grm. of the sample are mixed with 8·5 c.c. of methylated ether at 18° C. in a test-tube, which is then closed and shaken vigorously. Pure cocoa-butter will generally dissolve without heating, but if not, solution is effected using the least possible amount of heat.

The tube is then set aside and the manner of crystallisation noted.

Pure cocoa-butter will often not separate unless the temperature is reduced to about $10°$ C., and in any case it separates in small ball-like tufts, first at the bottom and gradually up the side of the tube, leaving a *bright solution*.

Five per cent. of beef fat, or less of beef "stearine," results in the separation of flocculent masses, and the solution *remains turbid*. In such cases the precipitate is examined microscopically. If the precipitate is due to beef fat, it will *not* go back into solution by shaking at $18°$ C., which will be the case with the deposit from genuine cocoa-butter.

It should, however, be noted that some of the modern cocoa-butter substitutes known as "green butters" and Borneo tallow are not possible of detection in admixture with cocoa-butter by means of this test.

Estimation of Stearic Acid by Hehner's Method.

The following method becomes useful when a quantitative determination of the actual stearic acid present in a mixture of fatty acids is required. It is particularly of use in ascertaining whether small quantities of beef " stearine " are present with vegetable fats, with the exception of those which contain appreciable quantities of stearic or higher acids in their glycerides (such as shea nut oil, cocoa-butter, etc.).

Method of carrying out the test.—The fatty acids from 10 grm. of the sample are prepared as directed under the Titer test (p. 14), and from 0·5 to 1·0 grm. (if solid) to 5·0 grm. (if liquid) are weighed into a small, light, tared flask and dissolved in about 100 c.c. of alcohol which has been

saturated at 0° C. with pure stearic acid. The flask is placed in an ice-bath over-night, after which the contents are shaken and again placed in the bath for a short time. If crystals are formed the liquid is then syphoned out (with the flask still in the ice-water) by means of a tube the end of which is covered with a small mat of fine linen. The flask and crystals are rinsed twice with about 10 c.c. of stearic acid alcohol solution (also at 0° C.), the rinsings being syphoned out by the tube. The linen is then rinsed into the flask with a few drops of hot absolute alcohol and the flask and contents dried and weighed. A small correction has to be deducted for the traces of stearic acid left in the flask from the stearic acid alcohol rinsings. For exactitude this should be determined on the flask used, but the correction of 0·005 grm. as given by Hehner is sufficient for ordinary purposes.

Hehner found beef " stearine " to contain about 50 per cent. of its fatty acids as stearic acid, arachis oil about 7 per cent ; while other liquid vegetable oils, and coconut oil gave no crystals at all, cotton - seed " stearine " gave about 3 per cent.

The stearic acid solution is prepared as follows : About 3 grm. of pure stearic acid are dissolved in 1 litre of strong alcohol in a stoppered bottle which is then stood in an ice-bath overnight, submerged np to the neck. The saturated liquid is separated by means of a syphon while the flask is in the ice-water. A small piece of muslin should be tied over the mouth of the syphon which dips into the bottle in order to prevent any solid particles passing over. As syphonage is often slow, it is advisable to connect the receiver to a suction pump and create a *small* reduction in pressure.

Glycerol.

As particular methods for the determination of glycerol have become official these methods only are here described, though, like all standardised methods, they are necessarily rather over-burdened with detail.

METHODS OF CRUDE GLYCERINE ANALYSIS RECOMMENDED BY THE INTERNATIONAL COMMITTEES.

(Abstract from their report.)

Sampling.

The most satisfactory method available for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler, then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled. Glycerine which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken, including any deposit.

Analysis.

(1) *Determination of free caustic alkali.*—Weigh 20 grm. of the sample into a 100 c.c. flask, dilute with

approximately 50 c.c. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid and titrate with normal acid. Calcuate to percentage of Na_2O existing as caustic alkali.

(2) *Determination of ash and total alkalinity.*—Weigh 2 to 5 grm. of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

(3) *Determination of alkali present as carbonate.*— Take 10 grm. of the sample, dilute with 50 c.c. distilled water, add sufficient N/1 acid to neutralise the total alkali found at (2), boil under a reflux condenser for fifteen to twenty minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and titrate back with N/1 NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_3O found in (1). The difference is the percentage of Na_2O existing as carbonate.

(4) *Alkali combined with organic acids.*—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

(5) *Determination of acidity.*—Take 10 grm. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with N/1 NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 grm.

(6) *Determination of total residue at* 160° C.—For this determination the crude glycerine should be slightly alkaline with Na_2CO_3 not exceeding the equivalent of 0·2 per cent. Na_2O, in order to prevent loss of organic acids. * To avoid formation of polyglycerols this alkalinity must not be exceeded.

Preparation of glycerine.—Ten grm. of the sample is weighed into a 100 c.c. flask diluted with water and the calculated quantity of N/1 HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petrie or similar dish 2·5 in. diameter and 0·5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mgrm.

Evaporation of the glycerine.—The dish is placed on a water bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate ¾ in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially

open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

An addition of 0·5 to 1 c.c. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours is required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1·5 mgrm. per hour is obtained.

Corrections to be applied to the weight of the total residue.—In the case of acid glycerine a correction must be made for the alkali added. One c.c. N/1 alkali represents an addition of 0·022 gramme. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight, multiplied by 100, gives the percentage of *total residue at* 160° C.

Preserve the total residue for the determination of the apparent glycerol content (p. 68).

(7) *Organic residue.*—Subtract the ash from the

total residue at 160° *C.* Report as organic residue at 160° C. (Note : It should be noted that alkaline salts of organic acids are converted to carbonates on ignition and that the CO_3 radicle thus derived is not included in the organic residue.)

(8) *Moisture.*—This test is based on the fact that glycerine can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride.

Two to 3 grm. of very pure bulky asbestos freed from acid soluble material, which has been previously dried in a water oven, is placed in a small stoppered weighing bottle of about 15 c.c. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1·5 grm. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about forty-eight hours. At lower temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

BICHROMATE PROCESS FOR GLYCEROL DETERMINATION.

Reagents required.

(A) *Pure potassium bichromate* powdered and dried in air free from dust or organic vapours at 110° to 120° C. This is taken as the standard.

(B) *Dilute bichromate solution.*—7·4564 grm. of the above bichromate (A) are dissolved in distilled water and the solution made up to one litre at 15·5° C.

(c) *Ferrous ammonium sulphate.*—Dissolve 3·7282 grm. of potassium bichromate (A) in 50 c.c. of water. Add 50 c.c. of 50 per cent. (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) *Silver carbonate.*—This is prepared as required for each test from 140 c.c. of 0·5 per cent. silver sulphate solution by precipitation with about 4·9 c.c. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used ; any excess of alkali carbonate prevents rapid settling). Settle, decant and wash once by decantation.

(E) *Subacetate of lead.*—Boil a pure 10 per cent. solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) *Potassium ferricyanide.*—A very dilute solution containing about 0·1 per cent.

The Method.

Weigh 20 grm. of the glycerine, dilute to 250 c.c. and take 25 c.c. Add the silver carbonate, allow to stand with occasional agitation for about ten minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 c.c. and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air dry filter into a suitable narrow-mouthed vessel, rejecting the first

10 c.c., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c.c. is ample.) Occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerine should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 grm. of the powdered potassium bichromate (A). Rinse down the bichromate with 25 c.c. of water and stand with occasional shaking until all the bichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapours, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (c), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 grm. glycerol = 7·4564 grm. bichromate.
1 grm. bichromate = 0·13411 grm. glycerol.

Notes.

(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one fifth and the basic lead acetate to 0·5 c.c.

(4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

Instructions for calculating Actual Glycerol Content.

(1) Determine the apparent percentage of glycerol in the sample by the above process as described.

(2) Determine the total residue at 160° C.

(3) Determine the bichromate value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol.

Examination of Oils and Fats for Various Impurities.

(A) *Moisture.*

In the case of neutral oils or fats it is usually quite sufficient to dry 3 to 5 grm. in a tared dish or large flat weighing-bottle at 105° C. to constant weight, weighing every half-hour until a minimum is reached. In dealing with oils and fats which are specially prone to oxidation, such as the drying oils, it is preferable to place the oil in a long test-tube, which is weighed together with a finely drawn-out tube reaching to the bottom and through which a current of dry CO_2 can be

passed. About 10 grm. of the oil are weighed into the tube, which is then heated in a slanting position in an oil or salt bath at $105°$ C., passing a slow current of CO_2 both during the heating process and until the oil has become cool. The heating is continued until the tube ceases to lose weight.

When the oil or fat contains any marked quantity of free fatty acids, which are of a volatile nature, the estimation of moisture is rather difficult. In this case a few grammes of the oil may be placed in a dish containing a known weight of sand and the mixture allowed to dry over sulphuric acid in a desiccator, or some of the oil may be filtered through two or three layers of dry thick filter-paper, and equal quantities of the filtered and unfiltered sample dried side by side at $105°$ C., the difference between the two losses of weight being taken to be that of the moisture present. It is assumed that the two quantities lose an equal weight of volatile acids, an assumption which is, however, not strictly true, the error increasing with the percentage of water present.

(B) *Non-fatty Matter.*

Carelessly treated oils may contain non-fatty constituents, which, in animal fats, will be tissue derived from the rendering of the fat, or, in vegetable oils, matter which has passed through the presses or extractors and has not been properly removed afterwards, or traces of soaps arising from refining processes. The quantity present is easily estimated by dissolving the oil in petroleum ether and filtering through a tared filter, after which the filter is placed in an extractor for a short time and then weighed.

(c) *Metallic Impurities.*

Traces of various metals or their compounds, usually as soaps, are also found in oils and fats. These may be :

(1) *Copper*, arising from the action of the fatty acids on copper containers, or purposely added as a colouring material, as in the case of olive oil.

(2) *Lead and zinc*, usually from containing vessels lined with these metals.

(3) *Lime,*
    Magnesia,   Usually the result of some refining
    Soda,   process, by which the free fatty
    Potash,   acids have been removed.

(4) *Iron* as an impurity from tanks or as a natural constituent of some oils and fats.

In order to separate these impurities from the oil or fat, two methods may be employed :

(*a*) About 20 grm. of the sample, melted if necessary, are shaken in a separator with 50 c.c. of 10 per cent. nitric acid, and allowed to separate. The aqueous layer is drawn off and evaporated to a small bulk and examined by the usual qualitative tests. This method may also be made quantitative if desired. Iron, copper and lead may be estimated colorimetrically.

(*b*) Ten grm. of the oil are incinerated in a porcelain dish by a method due to M. Delecoeuillerie. For this purpose the dish is placed on a sand-bath and a cone of ash-free filter-paper placed in the oil, point upwards. As soon as the fat has reached the volatilising point, a light is applied to the point of the filter-paper, when the burning of the fat is accomplished very simply, the last traces of carbon being burnt off over a Bunsen flame or in a muffle.

(5) *Sulphur.*—As carbon bisulphide is used as a

solvent in the extraction of oils, traces of sulphur may be present from this, as well as from other sources. It may be detected by saponifying 5 to 10 grm. of the sample, and adding to the solution of the soaps a small quantity of an alkaline solution of a lead salt, when, in the presence of sulphur, a *brownish colouration* will be produced.

(6) *Arsenic.*—A quantity of the oil is shaken out with nitric acid, as described above, the acid liquid being then concentrated to small bulk and Reinsch's test applied. If a positive reaction be not obtained, the examination should be repeated with the Marsh test as laid down by the Joint Committee (Journ. Soc. Chem. Ind., 1902, vol. xxi, p. 93).

(D) *Hydrocyanic Acid.*

A few c.c. of the oil are gently heated in a test-tube, in the mouth of which has been placed a strip of filter-paper, which has been dipped, first in a weak alcoholic solution of guaiacum resin, and secondly, *without drying,* in a 1 per cent. aqueous solution of copper sulphate. If hydrocyanic acid be evolved from the oil the paper develops a *violet stain.* The same test may be applied to the detection of the acid in oil cakes, in which case some of the ground cake is moistened with water and allowed to stand for a short time before testing, as in these cases the production of the acid is usually due to the presence of a cyanogenetic glucoside. The occurrence of these glucosides in feeding stuffs has been carefully investigated by Henry and Auld (Journ. Soc. Chem. Ind., 1908, vol. xxvii, p. 428). The following method for the determination of hydrocyanic acid as given by them may be used :

A convenient quantity of the product is rapidly

ground and placed in an extractor and exhausted thoroughly with hot alcohol. The alcohol is then distilled from the extract and the residue mixed with 50 c.c. of water and 10 c.c. of 10 per cent. hydrochloric acid. This mixture is then steam distilled until hydrocyanic acid ceases to pass over.

In the distillate the acid is estimated by adding a slight excess of sodium bicarbonate and then standard iodine solution until the solution is just faintly yellow.

Then since $HCN + I_2 = HI + CNI$, it follows that 1 c.c. of $N/10$ iodine $= 0\cdot00135$ grm. of HCN.

The Kinds of Oils and Fats commonly employed in various Manufactures.

It may possibly be of some assistance to indicate briefly some of the oils and fats which are most commonly employed in the manufacture of certain fatty foods, or of materials in which an oil or fat forms an important constituent. It must not, however, be supposed that in the following category are included all the materials which may be used, these being merely set out as a guide.

Chocolate.—Cocoa butter, coconut and palm kernel, " stearines," Borneo tallow, Japan wax, shea nut " stearine," and, in fact, any hard, solid vegetable fat. The solid animal fats were used in the past, but very little at the present day.[1]

Biscuits and cakes.—Butter fat, coconut oil, palm kernel oil, and mixtures of cotton-seed oil and beef " stearine," lard, premier jus, oleo oil, liquid vegetable oils, and margarines which may contain mixtures of the above. Hard vegetable fats, particularly coconut " stearine," are commonly employed in " puff " biscuits.

[1] The so-called " cream " of chocolate creams does not contain any oil or fat, but is chiefly a mixture of glucose and starch.

Ice wafers.—The layer of so-called " icing " usually consists of a mixture of coconut oil and icing sugar intimately incorporated while cold.

Marzipan.—This substance should consist of ground almonds and sugar only, but it will be necessary to look for other nut and kernel oils, as cheaper nuts and kernels are often substituted for the almond.

Caramels.—The fat usually present is butter fat, part of which may arise from the condensed milk used. Sometimes coconut oil and " stearine " and other fats are used, but are less suitable.

Toffee.—Chiefly butter fat or coconut oil, but sometimes margarine fats.

Tinned food packing oils.—Sardines and similarly preserved fish should be packed in olive oil, but cheaper substitutes, especially arachis and cotton-seed oil, are used in less expensive varieties.   In examining such oils, *after use*, it is to be remembered that traces of fish oil will be almost certainly present (see Henseval and Deny, abstract, Analyst, 1904, vol. xxix, p. 115).

Salad oils.—Any refined liquid vegetable oil, which does not deposit " stearine " on standing.

CHAPTER III.

THE methods and tests given in the previous chapters will, in general, be found sufficient for the examination of edible oils and fats in ordinary everyday work.

Stress is again laid on the necessity for the use of the *greatest care* in carrying out these methods, and for attention to *details,* as the methods themselves are often of an empirical nature, and so dependent on conditions that a deviation from the stated procedure will often lead to error. This is no doubt a common cause of the private condemnation of useful methods. The descriptions given are, in our opinion, sufficiently full to contain all the necessary detail, without being burdened with undue elaboration.

In the sphere of analysis of natural products, such as oils and fats, it will certainly be the case that no analytical method is infallible in its results, but because a method or test breaks down in certain isolated cases, it is no reason why, in the vast majority, its indication should not be received with due weight. There is, unfortunately, a type of mind which sees the exception and allows it to bulk so large, that the vista of agreement is entirely obliterated.

The analytical methods for oils and fats are some-

what of the nature of detective aids to common-sense, and only a just appreciation of their results will lead to success.   It is when they are regarded as fetishes, or interpreted in an inflexible manner, without due regard to the underlying principles, that disaster follows.

To give a general scheme for the examination of edible oils and fats would be, in the nature of things, impossible.   New oils are always appearing, and well-known ones, on account of better methods of refinement, are brofight into use for purposes for which, hitherto, they may have been considered impossible. Further, in our present state of knowledge, there are many oils and fats for which we have no distinctive reactions, or which possess no such characteristic features as would provide any sure guide to their presence, so that when a mixture of oils is the subject of examination, it is by no means always the case that its composition can be elucidated.

We have, on page 79, taken three general cases which may commonly arise, and have pointed out with the greatest brevity and diffidence that which is, *in our opinion*, the simplest method of attack.   To supplement these we have appended a number of examples which may indicate how analytical results are interpreted.

Before passing to these, however, we again set out, even at the risk of repetition, the general value and meaning of the methods and tests described in the last chapter.   Under each oil and fat in the following chapters there are given, as far as possible, the special tests or characteristics by which any such may be recognised, and when any particular oil or fat is suspected, reference should be made to the table of values appended, for further guidance.

(1) *Saponification value.*—This value gives a clear

idea of the mean molecular weight of the glycerides
present (p. 21).

The greater number of oils and fats have saponifica-
tion values between 190 and 200 and chiefly between
192 and 197; values higher than 200 are possessed by
the coconut oil group and butter, and some few fats,
such as Chinese vegetable tallow, porpoise jaw oil, the
chalmugra group, mafura tallow, ochoco fat, Japan
wax and dika fat.   On the other hand, perilla and
castor oils, shea butter and djave butter fall below
190 as a rule, and particularly the rape oil group, which
falls below 180.

(2) *Iodine value.*—This is a measure of the un-
saturated glycerides or acids, and when applied to a
known weight of the unsaturated acids themselves,
furnishes very clear information as to the actual nature
of those present (see p. 24).

High values characterise the liquid vegetable fats.
Perilla oil is the highest known (206), followed by the
drying oils (120–200), and the semi-drying oils such as
cotton, soja, etc. (100–140), then the rape oil group
(95–120) and non-drying oils (80–110).   The fish oils
range from 100–195, while the solid vegetable fats lie
in the neighbourhood of 40–65 (except the coconut
group), followed by butter fat at about 30–35, and the
coconut oil group from 5–25.

(3) *Refractometer value.*—This physical test is largely
of confirmatory value to the last, as in nearly all cases a
high value corresponds to a high iodine value.   Its indi-
cations, however, do not vary between such wide limits
as the iodine value for any particular oil or fat, so that
its indicative value is perhaps somewhat greater (p. 17).

The relation of these three values for a number of
different oils and fats is given on the annexed chart.   In
the case of mixtures, each constituent will affect the total

REFRACTIVE INDEX at 40°C.
ZEISS BUTYRO-REFRACTOMETER

COCONUT OIL
PALM KERNEL OIL
PALM OIL
CHINESE VEGETABLE TALLOW
COCOABUTTER
LARD
OLIVE OIL
SHEA NUT OIL
SUNFLOWER OIL
COTTON SEED OIL
RAPE OIL
SESAME OIL
MAIZE OIL
SOJA OIL
POPPY SEED OIL

35 40 45 50 55 60 65 70

IODINE VALUE

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140

SAPONIFICATION VALUE.

260 255 250 245 240 235 230 225 220 215 210 205 200 195 190

value found for each of the above three constants proportionately to its amount present in the mixture.

(4) *Reichert-Meissl-Polenske-Kirschner value.*—This is fully discussed under "Butter and Margarine," and gives very close results for the amounts of coconut, palm kernel oils, and butter fat present in admixture with other fats or oils, with the exception of cohune oil, which, analytically, behaves like coconut.

(5) *Acetyl value.*—The *true* acetyl value is the measure of the hydroxylated glycerides present, though, as Lewkowitsch points out, it is not strictly a constant, but a variable. Some oils, such as safflower, rape, etc., and the fish oils, are characterised by high acetyl values, so that in these cases it provides a distinct help in confirming their presence in mixtures (p. 28).

(6) *Bellier's test,* followed by *Renard's test,* gives exact information as to the presence and amount of arachis oil in a mixture of other liquid oils. Bellier's test, however, is useless in the presence of nearly all solid fats, both animal and vegetable, and the *quantitative* determination of arachis oil by Renard's test is, in such cases, practically impossible, and even the *qualitative* determination of the presence of the oil necessitates very great care (pp. 30 and 34).

(7) *Acid value.*—This is only a measure of the free fatty acids, and as such gives information as to the condition of an oil. It has no bearing on the composition of a mixture (p. 41).

(8) *The Hexabromide test.*—This test, used in a qualitative manner, is of value in determining the presence of fish oils and drying oils in admixture with other liquid vegetable oils, and to a certain extent gives evidence as to the presence of rape oil (p. 42).

(9) *The Lead-salt-ether method.*—This process is really a preliminary to further investigation. By its means

the unsaturated fatty acids may be separated, almost quantitatively, from the saturated acids. As a consequence, the presence of unsaturated acids other than oleic may be determined by means of the iodine value. The modification of Tortelli and Fortini allows of the detection of rape oil in the presence of practically all other fats (p. 38).

(10) *Unsaponifiable matter.*—This determination gives evidence, when the quantity is above normal, of the presence of mineral oils, waxes, etc. Apart from these, when high, it points to the presence of shea butter, which may contain 5 to 10 per cent., and in certain cases it may be the only means of detecting this fat (p. 44).

If the liquid after titration for the saponification value be diluted with water, the production of turbidity will indicate mineral oils or paraffin wax. Shea butter, on the other hand, usually gives but a slight turbidity, and the precipitate (if any) is sticky and remains at the bottom of the flask.

(11) *Phytosteryl acetate test.*—This too much neglected test is practically infallible in its indications of vegetable oils or fats in admixture with animal fats, but the reverse process, namely, the detection of small quantities of animal fats in vegetable oils, is not possible except by the use of the dibromide method (p. 44).

(12) *Optical activity.*—The importance of this test lies in its indication of certain poisonous oils, and its determination should never be neglected when examining unknown mixtures intended for edible use (p. 17).

(13) *Colour reactions*: (a) *Halphen's reaction.*—This indicates cotton-seed oil and kapok oil. In the case of the former it can generally be made fairly quantitative. The test seldom fails for cotton-seed oil, except when the oil has been subjected to certain rare treatments. When only a doubtful result has been obtained,

using the oil itself, more distinct indication will often be obtained on repeating the test with the fatty acids prepared from the oil (p. 52).

(b) *Baudouin's reaction.*—This is practically typical of sesamé oil. Certain rancid oils sometimes give a doubtful reaction, and in such cases the test should be applied to the fatty acids (p. 53).

(c) *Becchi's test.*—The modification of this test, proposed by Millau, is probably the only means of detecting kapok oil in admixture with other oils. It serves also to distinguish this oil from cotton-seed oil.

(14) *The microscopical examination of the deposit from an ethereal solution of fats.*—By this means the presence of beef and lard fats may be determined in the presence of liquid oils and of some solid vegetable fats. It also serves to determine the presence of beef fat in lard and *vice-versâ*. Such solid vegetable fats as shea butter are not distinguishable by this test from animal fats (p. 56).

(15) *Stearic acid* (Hehner and Mitchell's method).— By this method the actual separation of stearic acid is accomplished, and if the content in stearic acid of any fat be known, a good quantitative idea of the amount present in admixture with other oils or fats, not containing stearic acid, can be obtained (p. 59).

Three Typical Cases.

Case 1.—*A sample of oil guaranteed pure.*—It is required to say whether the description be true.

Procedure.—Determine the saponification value, and on completion of the titration, dilute well with distilled water and carefully note if there be any turbidity which would indicate unsaponifiable matter, such as mineral oils or waxes. Then determine the iodine and refractometer values, and compare these with the values

given for the oil. If *not normal*, take into consideration the cheapest possible adulterants of similar nature which could account for the abnormality (see current price lists in trade journals), and apply characteristic tests (if any) for such. If no characteristic tests are available, and the figures are so abnormal as to lie outside the known values of the oil in question, it is probably safest, if no further information be available, to return the oil as *abnormal in composition*.

If the figures be *normal* the sample may be pure, but in expert adulteration, additions will be chosen which will fall within the usual limits for as many of the values for the real article as possible, and the analyst must therefore consider what adulterants will fulfil these requirements, and will make such tests as will verify or disprove such suppositions. For instance, Bellier's test for arachis oil in olive oil, etc., the hexabromide test for drying oils in non-drying oils and so on. Taste and odour are sometimes of value for suggesting possible adulterants, but present-day oil refining has largely discounted the value of these tests, and in any case they require experience. The odour is best obtained by rubbing the sample in the hands. In the case of oils extracted from manufactured products, or oils which have been used for preserving fish, etc., as in the case of sardines, it must be remembered that traces of some other oil may have been extracted with the chief product, so that, for instance, fish oil may quite possibly be found in olive oil which has been used for sardine packing. See also p. 73.

CASE 2.—*An unknown oil or fat, but known to be not a mixture.*—If *liquid*, it may be presumed to be a vegetable oil (exceptions—lard oil and fish oils). Determine the iodine value, for as vegetable oils range from 79 to 206, this will best help to fix the probable

nature of the oil. Such oils as are thus indicated must then be followed up by all possible characterising tests. For fish oils see p. 273 ; limpidity and optical activity may also help.

If *solid*, the fat may be vegetable or animal, in which case determine the saponification value, as this will distinguish coconut and palm kernel oils, butter and allied fats. Then determine the iodine value, and, if necessary, apply the modified Björklund's test, as this will distinguish beef and lard fats and shea butter (examining deposit, if any, microscopically) from cocoa butter, certain illipé fats, etc. Shea butter can only be distinguished, in the last issue, from lard and beef fats, by the percentage of unsaponifiable matter and by the phytosteryl acetate test.

As regards the large number of vegetable tallows and solid fats, it is only possible to rely on the appearance of the sample and its analytical figures to arrive at a possible solution.

CASE 3.—*A mixture of edible fats*.—Some of the principal cases of mixed edible fats will be dealt with under "Margarine" (p. 129). In attempting to give the composition of a mixture, the greatest weight should be given to those results which can be determined with the greatest accuracy. For instance, the saponification value is a most exact figure, and its indications should not be allowed to be set aside for any other consideration, *i. e.* a value appreciably over 200 indicates the presence of glycerides of the lower fatty acids, the source of which must be accounted for in spite of the fact that the interpretation tentatively derived from all other analytical figures is inconsistent with it. Again, the Reichert-Meissl-Polenske-Kirschner values are of great accuracy in regard to the quantities of coconut, palm kernel and cohune oils, butter and rarer fats which

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may be present in a mixture, and they must be given due weight. The various colour tests and the hexabromide test are, in themselves, only indications of the presence of certain oils and fats, and no deduction as to quantity (with the possible exception in most cases of cotton-seed oil) should be made, but when a certain oil or fat is thus known to be present, its average figures can be employed to determine how much can possibly be present, in order to fit in with the general results obtained. The deposit (if any) from ether solution should be examined microscopically, as small quantities of beef "stearine" are used to stiffen softer vegetable fats. If small quantities of vegetable fats or oils are suspected in animal fats, and the figures obtained are not sufficient in themselves to certify to such addition, or if no really characteristic test for vegetable oils has been given (even cotton-seed oil may be so treated as to give such a slight reaction that small quantities might be passed over), the phytosteryl acetate test must be applied, always with care to ascertain the presence of paraffin wax added for the purpose of nullifying the test.

For the purpose of illustrating the foregoing principles, the following examples of some typical cases which may arise are given. They consist partly of actual problems which have arisen in the course of work, and partly of theoretical cases, so arranged as to illustrate the method of procedure and the deductions to be made from the results obtained. In giving such examples, we are perfectly aware that the results which we arrive at are not always the only possible ones; they are based on the methods which we have given only, and it is quite probable that, if a much greater number of determinations were made, somewhat more exact ideas might be obtained. The deductions which we have

made are, we believe, fully justified from the nature
and history of the samples examined and by the
general tendency and bearing of industrial processes.
By taking as a basis of calculation the extreme analytical
limits, and by working out all the permutations and
combinations of possible constituents which may arise
therefrom, it would probably be quite possible to find
half a dozen different solutions in some cases to the
following problems. The ordinary investigator will,
however, be quite safe, in the great majority of cases,
in working out his problems using the typical figures
for those oils and fats which he has found to be present,
and it is for his guidance that these examples have
been worked out. With the ultra-critical side of the
question we have no concern, as they are intended
rather to exemplify the methods of interpretation than
to provide a field for criticism.

Case 1.—*Olive Oil, guaranteed pure.*

Iodine value . . . . . 82·0
Refractometer number . . . 56·0
On cooling the oil became turbid at $2°$ C.

Colour and appearance normal.

Of the above figures, the iodine value is not
abnormal, the refractometer number and turbidity
temperature are quite normal, and relying on these
figures alone, the oil would have been passed as pure,
but as no olive oil should be passed without applying
Bellier's test, it was therefore tried, and a heavy per-
manent crystalline precipitate, reappearing after heating
and cooling the solution, was obtained, and by carrying
through Renard's test about 50 per cent. of arachis oil
was found to be present.

Case 2.—*Cocoa-butter, guaranteed pure.*

Saponification value	.	.	.	204·8
Iodine value	.	.	.	27·3
Refractometer number	.	.	.	44·2

Björklunds test gave rapid crystallisation from the ether, and the precipitate was not soluble at 20° C. Microscopically the insoluble crystals has the appearance of beef fat.

The sample was hard and brittle, and smelt strongly of cocoa-butter.

Inferences.—The high saponification value indicated the presence of coconut or palm kernel products. If, however, the *oils* had been present, the melting-point would have been too low and the fat soft in character. The presence of the " stearines " was therefore inferred. Now the saponification value of either coconut or palm kernel " stearine " is 250, and from this figure and the normal value for cocoa-butter (194) 20 per cent. of one of these " stearines " is calculated. As it is not possible to arrive, in any simple manner, at any certain conclusion as to which of the two " stearines " might be present, it was taken to be coconut " stearine." This has an iodine value of 5, and taking 20 per cent. to be present in the mixture, it follows that the remaining 80 per cent. has an iodine value of 33, and, by similar calculation, a refractometer number of 46·5. These figures would pass for cocoa-butter, but as beef fat has been demonstrated, a small percentage is evidently present, but the actual amount could only be arrived at by making up standard mixtures and comparing the volume of the precipitates deposited from ether solution or by the method of Hehner and Mitchell (p. 59).

The composition of the mixture was given as :

Coconut " stearine "	.	.	20 per cent.
Beef ,,	.	.	5 ,,
Cocoa-butter	.	.	75 ,,

Case 3.—A Lard Substitute.

Saponification value	.	.	.	194·0
Iodine value	.	.	.	95·5
Refractometer number	.	.	.	56·0

The sample was a soft plastic fat.

Inferences.—The saponification value showed that no glycerides of low molecular weight were present.

The iodine value shows the presence of a liquid vegetable oil, confirmed by the refractometer number.

Halphen's test was strongly positive, and on diluting down with an indifferent oil (until the reaction was below that given by the 20 per cent. standard) it was evident that about 80 per cent. of cotton-seed oil was present in the original sample. This high percentage of liquid oil necessitated the presence of a stiffening fat.

A solution of 2 grm. in 10 c.c. of ether gave a copious precipitate, which on microscopical examination was evidently from beef fat, and, as only a comparatively small quantity could possibly be present, it was necessarily beef " stearine." It was assumed therefore that only cotton-seed oil and beef " stearine " were present, and, calculating from the iodine values, the composition was returned as :

| Cotton-seed oil . | . | . | 85 per cent. |
| Beef stearine | . | . | 15 ,, |

Case 4.—A Sample of Coconut Oil.

Saponification value	. .	237·0
Iodine value	. .	25·2
Refractometer number	. .	39·5
Reichert-Meissl value	.	5·7
Polenske value	. .	12·6
Setting point	. .	76·0° F.
Free fatty acids	. .	3·5 per cent.

No precipitate was obtained from 2 grm. of the fat in 10 c.c. of ether when kept in ice for thirty minutes.

Inferences.—The case presented some difficulty in interpretation.

The saponification value suggested the presence of another fat, but sufficiently cheap available solid fats were negatived by the ether test.

Liquid vegetable fats were negatived by the setting-point, which is two to three degrees above the normal for coconut oil. Coconut or palm kernel " stearines " might be present, but were negatived by the refracto-meter and iodine values. All the figures are normal for coconut shavings oil, and the sample was therefore reported as such (see p. 151).

It may be useful to point out that liquid vegetable oils are excluded by the values obtained, though, at first sight, their presence might be inferred. To account for the saponification value found, a mixture of 70 per cent. coconut oil (iodine value 8·5) and 30 per cent. of liquid vegetable oil (iodine value 100) would be required, or else a mixture of 80 per cent. palm kernel oil (iodine value 14) and 20 per cent. of liquid vegetable oil. The iodine value in these two cases would be 36 and 31 respectively and are therefore much too high. Simi-larly the refractometer numbers would be 42 and 41 and are also too high, and if either of these were

adjusted to fit the found value, the saponification value, which is the most reliable figure, would show considerable discrepancy.

Case 5.—Oil extracted from Biscuits.

Saponification value	. 229·0
Iodine value .	34·2
Refractometer number	. 42·5

A solution of 2 grm. in 10 c.c. of ether gave a copious precipitate on cooling in ice, and the crystals, microscopically, were characteristically lard.

As the high saponification value indicated coconut oil or butter fat, the following determinations were made :

Reichert-Meissl value	. 6·7
Polenske value .	. 7·0
Kirschner value	. 1·6

These correspond to a mixture containing 50 per cent. coconut oil and about 2 per cent. of butter fat. The mean values for the saponification, iodine and refractometer numbers were taken, and from these it was found that a mixture of—

Coconut oil .	50 per cent.
Lard	. 48 ,,
Butter fat .	. 2 ,,

fits in well with the values found for the original sample. The above mixture is therefore very probably correct. The values for coconut or palm kernel " stearine " do not fit in at all well, and their presence may be therefore taken as negatived.

Case 6.—Oil from Oil Cake.

Saponification value	. 171·5
Iodine value .	98·3
Refractometer number	. 58·6

The very low saponification value pointed to rape oil, as no unsaponifiable matter was noted on diluting the solution. The only possibility which has to be accounted for is that of a mixed cake, and this possibility seems very doubtful unless the admixture was very small.

Halphen's test was negative.

The hexabromide test was quite typical of rape, and the solution cleared on the addition of ether.

The oil was therefore reported as being from rape cake.

Case 7.—A Sample of Oleo Oil.

Saponification value	. .	198·0
Iodine value .		50·8
Refractometer number		. 48·1

The presence of lard in the sample was practically excluded by a microscopical examination of the crystals obtained from a solution of 5 grm. in ether, and as the amount of the precipitate was very small, the presence of beef " stearine " was practically negatived.

Halphen's test was negative.

Baudouin's reaction was negative.

These results, taken together with the quite normal figures, practically establish the purity of the sample. In order to definitely exclude the presence of any vegetable oil, it would have been necessary to use the phytosteryl acetate test.

Case 8.—A Margarine Fat.

Saponification value .	.	196
Iodine value . .		. 76·0
Refractometer number	. .	. 52·5

Inferences.—The saponification value excludes coconut

oil products and butter fat, except in traces, and the iodine value suggests liquid vegetable oils.

The Halphen reaction was strongly positive, and the quantity of cotton-seed oil present was roughly indicated as between 30 and 60 per cent.

As a solid fat must necessarily be present, 5 grm. were crystallised from ether and the precipitate on microscopical examination indicated the presence of lard. As *no beef crystals* were found premier jus and beef " stearine " were practically excluded, but *not oleo oil*.

As the unsaponifiable matter was only 0·3 per cent. the presence of shea butter as against lard was negatived.

As this examination was made at a time when lard was higher in price than beef fat, it seemed exceedingly probable that oleo oil might be present, but, on account of the wide limits which it was necessary to assign to the amount of cotton-seed oil present, the actual incorporation of oleo oil can only be deduced inferentially. For instance, the composition might be worked out as follows : supposing 30 per cent. of cotton-seed oil to be present in the mixture, the iodine value of the other 70 per cent. would be 61, which value would be quite correct if it were all lard, but the quantity of crystals obtained from the ether was too small for so large a percentage.

If 60 per cent. of cotton-seed oil be taken to be present, a residual iodine value of 25 is necessary, which is clearly impossible. If a mean value of 45 per cent. cotton-seed oil be taken, a residual iodine value of 48 is obtained, so that, by taking all these into consideration, it was quite justifiable to assume that both oleo oil and lard were present, and that the oleo was in excess of the lard. The composition was therefore returned as probably :

Lard .   .   .   .   .   20 per cent.
Oleo oil   .   .   .   40   ,,
Cotton-seed oil   .   .   .   40   ,,

Case 9.—An Adulterated Ghee.

Saponification value   .   .   .   219
Iodine value   34
Reichert-Meissl value   .   .   24·8
Polenske value   .   .   .   .   2·4
Kirschner value   .   .   .   .   17·0
Difference figure (Avé-Lallement)   .   + 12

Inferences.—The figures point to an addition of some solid fat (vegetable or animal), as the iodine value was too low for a liquid vegetable oil.

The Polenske value excluded coconut oil products, and the relation of the Kirschner value to the Polenske value confirmed this. The addition, therefore, was either lard, beef, or a solid vegetable fat. The microscopical examination of the deposit from ether breaks down completely in the presence of butter fat, and could not therefore be applied.

The presence of shea butter was excluded by a normal amount of unsaponifiable matter. The only solution of the problem lay in the use of the phytosteryl acetate test. The acetates at the fifth crystallisation melted at between 116° and 118° C., from which it was concluded that a solid vegetable fat, not improbably, from the nature of the product, one of the Bassia fats, was present. The percentage cannot be found except in a very approximate manner, but from 15 to 25 per cent. was inferred.

Examination of the Fatty Acids by Fractional Precipitation.

In certain cases it may be necessary to examine more closely the fatty acids which can be obtained from the sample under examination.

A full scheme cannot be given here, as such an examination does not form an ordinary analytical operation, and for such, reference must be made to larger text-books.

The following brief outline will give an idea of some methods of attacking the problem. The fatty acids are prepared from a large quantity of the fat by saponification with alcoholic potash or soda (about 15 grm. of caustic alkali and 250 c.c. of 90 per cent. alcohol to 50 grm. of fat). The alcohol is partially distilled off and the solution of the soaps poured into a large excess of water containing sufficient hydrochloric acid to decompose them, and the fatty acids allowed to rise and solidify. They are then skimmed off and placed in a large separating funnel and dissolved in ether, and the solution washed till free from hydrochloric acid. If any noticeable quantity of the acids refuse to dissolve in the ether, it is generally due to the presence of esters formed by incomplete saponification. The water is drained as much as possible, and the ethereal solution shaken with a little calcium chloride for a short time and filtered through a triple layer of thick filter-paper into a dry flask and the ether distilled off, the last traces being removed by blowing air into the flask, or, when unsaturated acids are present, by driving a current of hydrogen through the liquid.

It is sometimes advisable to re-melt the fatty acids at as low a temperature as possible, and filter through

dry filter-paper, taking care that no partial solidification
takes place during the process. From the fatty acids
so obtained, the unsaturated acids (oleic, linolic, etc.)
are separated by the lead-salt-ether method, the solid
acids being recovered from their lead salts by decom-
posing them in the usual way. The composition of the
unsaturated acids is ascertained by determining the
iodine value very carefully. Oleic acid absorbs two
atoms of iodine, linolic four atoms, etc., so that from
the weight of acids taken, and their iodine absorption,
the presence of one or more unsaturated acids can be
determined, and their proportion with fair accuracy.
For the resolution of the fatty acids, undoubtedly the
simplest method is fractional precipitation by magnesium
acetate as recommended by Heintz (Journ. prak. Chem.,
1855, lxvi, p. 1.) For this purpose, 40 to 50 grm. of the
fatty acids are dissolved in sufficient alcohol to keep
them in solution when quite cold. To this solution,
while hot, is added a boiling alcoholic solution of
magnesium acetate (about 1–2 grm. at a time) and the
solution allowed to cool and the precipitate filtered off.
To the filtrate a further addition of magnesium acetate
is made and the precipitate filtered off as before.
When no more precipitation takes place, the solution
is made alkaline with ammonia and more acetate added,
leaving the whole to stand twenty-four hours before
filtration. Any acids not then precipitated may be
thrown out by lead acetate, after rendering the solution
acid with acetic acid.

The various fractions are washed with alcohol, and
decomposed under ether with hydrochloric acid and the
fatty acids recovered. The mean molecular weight of
the fractions is then determined by saponifying with
N/2 alcoholic soda or potash (mere titration is not suffi-
cient on account of the tendency to form anhydrides),

and by this means a very good idea of the various acids present may be obtained.

When lauric acid and acids of lower molecular weight are present, they may be separated from higher acids by decomposing some of the original saponification mass (after distilling off the alcohol) with dilute sulphuric acid, and steam distilling till 1000–2000 c.c. have passed over, the acids being recovered from the distillate by extraction with ether, or by neutralising it and concentrating previous to acidification and extracttion. By converting these acids into barium salts, a considerable separation may be effected by boiling out with water, as saturated fatty acids up to capric acid are soluble. The fatty acids can then be liberated again and their mean molecular weights determined.

Separations carried out intelligently on the above lines will in most cases enable the investigator to arrive at the approximate composition of a fat or to determine the predominant fatty acids present.

CHAPTER IV.

ANIMAL FATS.

For practical purposes the analyst has to consider only two animal fats and their products, viz. beef fat and lard.

Beef Fat.

This is the product obtained from bovine animals. A very similar fat is obtained from the sheep, but as there is little difference analytically between this fat and true beef fat they will be treated as similar, as even to the expert their differentiation in presence of one another is practically a matter of guesswork. Beef fat is more valued on account of its superior taste and smell.

Immediately the animal has been slaughtered the fatty portions are usually removed, and treated as follows : For products intended for the manufacture of oleo-margarine, the fat of the heart, caul and kidneys is chilled quickly to remove animal heat and rendered at as low a temperature as possible (100° to 120° F.). The clear fat which runs out is termed " *Premier jus.*" This, with or without various clarifying treatments, such as washing with a solution of common salt, is allowed to " grain," and is then " bagged " up (2 to 3 lb. per bag) and submitted to hydraulic pressure. The fat which is so expressed sets to a soft buttery consistency and is known as " *oleo* " or " *oleo oil,*" and is the product employed in the manufacture of margarine.

The residue in the bags is in the form of hard cakes known as " *oleo (or beef) stearine.*"

In cold weather, when a softer oleo oil is required, the pressing is not carried out so completely, the result being that both products are softer in character with a larger yield of " stearine." The process is reversed in warm weather. The various ways of, and reasons for, compounding these products will be found under the head of "Margarine." All the other fatty portions of the carcase not sold as beef are rendered in such a manner as to produce the maximum yield of fat. These form the various grades of tallow, the bulk of which go to the soap maker, but some of the finer grades are used for edible purposes ; the residual tissue, after the rendering of the premier jus, is worked up in a similar manner.

In the following paragraphs only the necessary practical tests for the examination and valuation of beef products are given in connection with their use for edible purposes. Such tests as would be necessary for soapmakers' work are not dealt with here.

The examination of oleo products for adulteration with other fats is not of great importance, as in our experience edible beef products are not as a rule sophisticated. If such examination be desired the methods given under lard may be employed. The analytical examination is rather directed to their valuation for definite technical processes. The point on which all such technical value turns may be summed up almost entirely under the heading of "consistency," which cannot always (paradoxical as it may sound) be adjudicated upon by the melting-point alone as usually determined. The analytical determinations which must be made are :

The iodine value, substantiated by the *refractive index* which give indications in the same direction, and

perhaps the *saponification value*, though the iodine
value is practically all that is necessary as it furnishes
a direct measure of the olein present, the content of
which (as a result of the methods of preparation) is the
distinguishing mark of these products.

The *free fatty acids* must be determined in connection
with observations on the taste and smell, as the presence
of more than 0·5 per cent. (calculated as oleic acid)
will produce a distinct burning sensation in the throat,
and render them unpalatable.

Consistency.—Attempts have often been made to
measure this most important property by the determina-
tion of an arbitrary figure obtained by some physical
means, but this has not proved at all satisfactory in
practice.

It is much better to determine the *points of incipient
and complete fusion* and to draw deductions from their
relation. For instance, if they are widely separated and
the fat divides during fusion into a distinct liquid and
solid portion, it is probable that the product is a
mixture which contains a proportion of high melting-
point " stearine," and the fat, therefore, will have a
structure consisting of hard granules embedded in a
semi-liquid matrix. On the other hand, a product which
melts within close limits and fairly uniformly will have
a more lard-like, plastic, and less granular structure.
The above are, of course, extreme cases, but are intended
to show how such observations may be employed to
assist the manufacturer to match two different consign-
ments when he is not able to settle the point by simple
observation. It is, of course, to be clearly understood
that in the case of sharp melting-points, the actual
temperature of fusion is to be taken into account, as
both beef " oleine " and beef " stearine " have sharp
melting-points, but will differ widely in the actual

temperatures of fusion. The determination of the solidifying point is of little value, as no very definite figure can be obtained, but the solidifying point of the fatty acids is fairly definite and is determined as described under Titer test and then gives similar information to the results of the melting-point determinations.

Such results taken in conjunction with the iodine value furnish all possible information obtainable for comparative purposes.

Oleo oil and premier jus are coarsely granular fats of attractive appearance. Beef " stearine " is usually in the form of broken press-cakes showing the marking of the bags, but if re-melted and solidified in moulds it has the appearance of stearine candles. The colour may vary from pale creamy white to yellow, bleaching with age. Oleo oil is usually slightly deeper in colour than beef " stearine."

The following figures will be sufficient guide to the examination of these products :

	Beef tallow.	Premier jus.	Beef stearine (oleo-stearine).	Oleo oil.
Melting-point ° C.	47–49·5	47–49	50–54	Variable
Solidifying point ° C.	32–37 (Indefinite)	32–35 (Indefinite)	47–50	Indefinite
Saponification value .	193–199	195–200	192–197	198–202
Refractive index (Zeiss butyro-refractometer at 40° C.)	47–49	47–48	46·5–47·5	47·5–48·7
Iodine value	38–44	38–45	18–25	40–50
Titer test ° C. .	43–45	42·5–44	48–51	—
Baryta values*—				
(a) Total	—	272·1	270·0	274·5
(b) Insoluble .	—	263·8	269·4	261·2
(c) Soluble	—	8.3	0·6	13·3
b − (200 + c)	—	+ 55·5	+ 68·8	+ 47·9

* *Avé Lallement.*

The free fatty acids vary, but when the fats are intended for edible use the amount should not exceed 1 per cent., and is usually not more than from 0·2 to 0·4 per cent.

Lard.

At the present day, lard must be taken as describing the whole of the fat derived from pigs. The fat is rendered in various ways, by which a variety of products are obtained which are classified under various grades in America, as follows :

(*a*) *Neutral lard*.—No. 1. This product is obtained from the " leaf " by rendering the chopped mass, after thorough cooling, at a temperature of 40° to 50° C., and is the variety almost entirely employed for the manufacture of margarine. No. 2 is obtained in a similar manner from fat derived from the back of the animal, and is used more particularly in biscuit manufacture, and probably to a certain extent in margarine.

(*b*) *Leaf-lard*.—This is obtained by autoclaving the residue left after rendering the " leaf or neutral lard," at steam heat.

(*c*) *Choice kettle-rendered lard*.—This is obtained by heating the residues left from the preparation of a " neutral " lard in open steam-jacketed vessels.

(*d*) *Prime steam lard*.—This term is applied to the renderings of almost all the other parts of the animal from which lard may be obtained—direct steam heat being used for the purpose. Any fatty residues which are left over are worked up under pressure, in order to produce low quality fats, usually termed " greases," which are not used for edible purposes. For a full description of these varieties, and of their composition and characteristics, see Lewkowitsch, ' Oils, Fats and Waxes,' vol. ii, 1909.

It may be necessary in practice either to examine lard for its purity or to detect it as a constituent of mixtures.

EXAMINATION OF LARD FOR ADULTERATION.—Unfortunately pure lard itself varies rather considerably in its composition, according to the part of the animal from which it is obtained and also with the manner in which the animal has been fed. It is therefore necessary to obtain actual evidence of adulteration and not to rely on simply abnormal figures.

Water.—This may be determined by drying a few grammes of the sample in a thin layer in the water oven to constant weight. The amount may also be determined fairly closely by observing the temperature at which the melted fat becomes turbid, as described by Polenske (Arb. a. d. Kaiserl. Gesundheitsamte, 1907, xxv, p. 505). The following figures have been obtained by this method by Fischer and Schellens :

Water per cent.	Turbidity, °C.
0·15	41·2
0·20	53·2
0·25	64·6
0·30	75·8
0·35	85·0
0·40	90·8
0·45	95·2

Iodine value.—This test is probably of some value as giving an indication of the purity of the sample, as a high iodine value will suggest the presence of some vegetable oil, providing that such admixture has not been compensated for by the addition of beef "stearine," but the iodine value of genuine lard seldom falls outside the limits of 48 to 66 per cent. Lards of American origin, according to Voigtländer, fall nearly always

between 61 and 66 per cent., tending usually to the higher value.

Refractive index.—This figure is of some little use, but only in conjunction with other tests, on account of its close proximity to that of beef fat.

Unsaponifiable matter.—As lard is often adulterated with a judicious mixture of beef fat and vegetable oils, which give no definite reactions, the examination of the unsaponifiable matter for the presence of phytosterol may be the only way in which the adulteration may be detected. Particular care must be taken that this test is not defeated by the addition of traces of paraffin wax, and precautions against this must consequently be taken (see p. 48).

Particular adulterants : Beef fat.—It is perhaps best to say at once that 5 to 10 per cent. of beef fat in lard cannot be detected with certainty, if at all. The presence of higher percentages may perhaps be arrived at by the microscopical examination of the crystals obtained from an ethereal solution of the fat (see p. 56) and by the Titer test.

Goske gives the solidifying point of a number of lards as lying between 24° and 29° C., with one or two exceptions, while in the case of lards adulterated with beef fat, solidifying points from 29·5° C. up to nearly 37° C. were obtained.

Undoubtedly the method of Hehner and Mitchell, in which the iodine value and stearic acid content of the mixed fatty acids are determined, may lead to useful indications, as they point out that a high iodine value and a high stearic acid content would suggest the presence of beef "stearine," as in genuine samples of lard the iodine value rises as the percentage of stearic acid falls. The following figures are given by Mitchell for pure lards (Allen's Organic Analysis, fourth edition, p. 318).

Iodine values.	Stearic acid, per cent.
57·5	16
61·2	13
61·2	6 to 7
63·6	7·4
65·6	9·9 to 10·6

Cotton-seed oil.—This may be detected by *Halphen's test*, the colour given being interpreted with care, as there is not the least doubt but that lard from pigs fed on cotton-seed meals sometimes gives a slight positive reaction. Positive reactions must therefore be considered carefully in connection with other figures. As *heated* cotton-seed oils give no colour with Halphen's test it is advisable, when a negative reaction has been obtained, to apply the *nitric acid test*, as recommended by Lewkowitsch :

For this purpose about 5 c.c. of the sample are mixed with 5 c.c. of nitric acid (sp. gr. 1·375) in a stoppered tube and violently shaken. Under these circumstances *cotton-seed oil* produces a *coffee-brown colour*, the production of which is not affected by previous heating of the oil. The test, however, does not show less than 10 per cent. Unfortunately, rape oil gives an entirely similar colour, but may be differentiated by the method given on p. 38 (Tortelli and Fortini).

Sesamé oil.—This may be detected by the *Baudouin reaction* (p. 53).

Arachis oil.—This may sometimes be detected by examining for arachidic acid, by Renard's test, after repeated recrystallisation, but if much " stearine " be present the results are doubtful.

Maize oil.—This oil may possibly be present as an adulterant when the presence of vegetable oils not giving specific reactions is suspected. As it gives a phytosteryl acetate of unusually high melting-point, this

test may be of distinct value in detecting the presence of this oil.

It may also be useful to obtain the iodine value of the *liquid fatty acids*, as they are particularly high (136 to 144) in the case of maize oil, while lard seldom gives a figure above 105.

Shea nut oil and its products (such as the " oleine") are now on the market to some extent as lard substitutes, and may therefore be expected to find their way into lard. The presence of these products, except in small quantities, may be fairly easily detected by the high unsaponifiable matter, a slightly lowered saponification value and iodine value, together with an increased refractive index.

Coconut oil offers but little difficulty in detection. Any appreciable quantities will greatly increase the saponification value and lower the refractive index and iodine value. Small quantities may be detected by a rise in the saponification value of an alcoholic extract as compared with that obtainable from pure lard under similar conditions. This is due to the fact that coconut oil is very much more soluble in alcohol than lard.

A determination of the Reichert-Meissl-Polenske value will confirm these results.

The greater majority of samples of lard will be found to give analytical figures within the limits of the following table :

Melting-point, °C. .	35	to	46
Solidifying point, °C.	25	,,	30
Saponification value .	193	,,	199
Refractive index (Zeiss butyro-refractometer at 40° C.)	49	,,	52
Iodine value . . .	57	,,	66
Specific gravity $\frac{99}{15}$ °C. .	0·860	,,	0·862
Free fatty acids (as oleic) .	0·1 %	,,	0·8 %
Unsaponifiable matter .	0·2 %	,,	0·4 %

General Considerations.

In detecting adulteration in lard only small quantities of other oils are likely to give great difficulty. It must be understood that the addition of liquid vegetable oils will in any skilful form of adulteration be masked by the addition of beef " stearine " in order to produce the necessary consistency. If, therefore, vegetable oils are suspected, the likelihood of this concurrence must be taken into account when considering the figures obtained. As in margarine, so in lard, almost any vegetable oil may be sought for at the present time. Attention is again drawn to the great value of the determination of the unsaponifiable matter (shea nut products) followed by the phytosteryl acetate test, as indicative of the vegetable oils in general, and of maize oil in particular, and also to the methods which are employed to defeat this latter test (traces of paraffin wax).

Lard Substitutes.

A variety of mixtures of fats, so blended as to resemble lard both in consistency and other properties, may be found on the market. The most common of these is a mixture of about four parts of some liquid oil and one part of beef " stearine." Some of these products contain a small quantity of starch, added in order to mask the tendency of the more liquid portion to separate. This type of mixture probably constitutes quite 90 per cent. of those offered for sale at the moment, but there is no doubt that shea nut products are coming on the market in large quantities and will begin to displace such mixtures.

"Compound" lards should be understood to be mixtures of true lard with other fats, but we have found products described as "lard compounds" in which no lard was present at all.

We feel that the analyst should be cautious in condemning such mixtures as fraudulent, as in most cases no fraud is intended, nor would it be to the prejudice of the purchaser. Refined coconut oil is commonly sold as " pure vegetable lard," and we see no reason to quarrel with such nomenclature.

Butter and Margarine.

It is scarcely too much to say that the examination of these two substances presents the most difficult problem which the oil analyst has to face. This is due to the extreme variation and complexity which may arise in the production of the latter, and to the wide natural variations of the former, coupled with the fact that adulteration usually consists in the admixture with it of certain quantities of the latter. While a knowledge of the products on the market, ruling prices, and indirect information often enable the investigator to solve the problem of margarine mixtures with reasonable certainty, there is, in a large number of cases, absolutely no method of arriving at proof that the constitution of any sample of butter-fat is due to sophistication and not to natural causes. This natural variation has brought the analyst into the uncomfortable and unscientific position of having to fix limits of variation in dealing with butter-fat, and the result, as always in such cases, is most unsatisfactory; but until some talisman be found which will distinguish the natural from the artificial, this state of affairs will probably continue. The authors, however, desire to express their decided opinion that little is gained by condemning the natural as artificial when reasonable evidence is available that the composition, on which the decision is based, is the result of natural causes

beyond the control of the human agent, and not simply due to inefficient or improper feeding, or unnecessary exposure of the cattle to adverse climatic conditions. There is no evidence whatever that an unusually small content of the glycerides of volatile and water-soluble acids due to natural causes renders butter-fat any the less digestive or nutritive, nor is the purchaser prejudiced thereby. In the present state of our knowledge it is better for the analyst simply to fall back on the recognised standard when there is no evidence to show that the composition is natural, and not to attempt to give any weight to his adverse decision by adding remarks as to nutritive value, etc., which are of doubtful utility.

As the examination of butter and margarine run to a certain extent on parallel lines, they will be considered together.

Sampling.

By far the greater number of discrepancies found in the analyses of different observers with regard to water content are caused by inefficient sampling and after-care of the sample. In sampling large bulks of butter or margarine, a piece about 2 in. long by 1 in. square is cut by means of a *thin* wire from the centre of the mass, and the piece, so cut, lightly pushed with the finger into a dry 6-oz. wide-mouthed stoppered bottle, in such a manner that a trace of the sample is left on the ground inner surface of the neck. A *well-fitting* stopper is inserted and carefully twisted round until it is well greased. This procedure is essential in order that none of the water from the sample when melted should pass between the stopper and the neck by capillary attraction. The bottles containing the samples are placed in water (or preferably in an incubator) at 38°to 40° C. until melted.

WATER.

Routine Method for a Number of Samples.

The estimation is carried out in large weighing bottles 2 in. deep and $1\frac{1}{2}$ in. wide, having no shoulders. The requisite number are dried in the water oven, together with a tare, and allowed to cool in the air or under a cover. They are then weighed in succession, and about 3 to 5 grm. of each sample rapidly poured in from the sample bottles, after the contents have been shaken vigorously to the consistency of cream. The series of bottles, having been re-weighed, are then placed in the water oven, the contents being thoroughly shaken round at intervals until visible water has disappeared. The bottles may then be tilted on one side, and turned round from time to time until the weight is constant. If the shaking be skilfully done the whole operation will only take from two to three hours.

Patrick's Method for Single Samples.

About 5 grm. of the sample are poured out into a platinum basin and gently heated, preferably about 6 in. above the flame of an argand or small bunsen burner. The contents of the dish are gently boiled, while shaking, until " hissing " ceases, when all the water will have been driven off. If properly carried out there should be no discoloration of the curd, and the results are quite as accurate as in the case of the foregoing method.

FAT.

The residue left after driving off the water in either of the above methods is exhausted five times with 20 c.c. of ether, allowing the residue to stand under the ether for at least a quarter of an hour at each extraction. The loss in weight after this treatment gives the fat present.

Curd.

The extracted residue is well stirred up with warm water, and brought on to a small tared filter, and washed till the washings are free from chlorides. The filter-paper is then dried and weighed. The increase is taken as " curd." It does not as a rule exceed 1·0 per cent.

Salt.

This is estimated by evaporating the washings from the curd estimation to a convenient bulk, and titrating with N/10 silver nitrate and potassium chromate in the usual way. Total mineral matter, if required, may be estimated by difference, that is, by subtracting the total weight of the water, fat and curd from the weight of the sample taken. Boric acid does not interfere with the salt estimation.

Quite recently attention has been drawn to the practice of some butter-makers of adding dried milk to butter. This is probably done in order to improve the flavour of butters which have " gone off " in cold storage. Without giving any opinion as to whether this practice is legitimate or not, we feel that in those cases in which the addition can be definitely proved it should not be passed over without comment, and it should be made clear to the consumer that an addition to the butter has been made, leaving it to him to decide whether such " renovated " butter is or is not sold to his prejudice as pure butter.

The presence of added dried milk can be easily detected by determining the lactose present. This is done by washing out the butter as described below under boric acid, making the aqueous extract faintly acid with acetic acid, filtering off the precipitated casein and titrating the filtrate against Fehling's solu-

tion, taking 10 c.c. of Fehling's solution to require 0·07 grm. of lactose monohydrate to reduce it (p. 314).

Pure butters seldom exceed 0·5 per cent. of lactose monohydrate, and any percentage much exceeding this limit points to the addition of dried milk to the butter.

PRESERVATIVES.

BORON COMPOUNDS.—For rapid routine tests, a portion of the sample about the size of a pea is melted in a small crucible lid on the water bath, one drop of strong hydrochloric acid added and stirred in with a rod, and then five or six drops of a saturated alcoholic solution of turmeric. A *rose red colour*, immediately forming as the edges dry, indicates the presence of boron compounds, the colour being changed to a purple green on the addition of a drop of ammonia.

The turmeric solution should be made by boiling about 50 grm. of turmeric powder with 250 c.c. of strong alcohol under a reflux condenser for at least an hour, and then filtering. This keeps well.

The above method will detect 0·02 per cent. of boric acid with certainty. If greater delicacy be required, a larger quantity of the butter must be rapidly boiled down in a basin, the fat poured off, and the residue incinerated, acidified with HCl, and evaporated to dryness, with a turmeric paper placed down the side of the basin and dipping into the liquid. If, as the paper dries, it turns a *rose red* colour, and this colour is changed to *blue-black* on moistening with ammonia, then boron compounds are indicated.

Estimation.—Twenty grm. of the sample are weighed in a small beaker, and washed into a separating funnel with petroleum ether and water, using two quantities of about 10 c.c. of ether and three quantities of 10 c.c.

of water. After standing, the aqueous layer, up to the casein, is run off into a small flask and 25 c.c. mixed with 6–7 c.c. of 1 per cent. phenolphthalein solution in strong alcohol.

The mixture is brought to the boil, and a distinct excess (2 to 3 c.c.) of N/10 NaOH added. The solution is titrated back with N/10 acid till colourless, and then adjusted to the neutral point by alternate additions of the acid and alkali, the solution being kept at the boiling point throughout the operation. Two grm. of mannitol are then added, the solution cooled and tiltrated with N/10 NaOH till just pink.

If the water content of the butter be not known it may be taken as 15 per cent., when the amount of boric acid will be—

Boric acid (H_3BO_3) per cent. $= X \times \dfrac{33}{25} \times 5 \times 0.0062$

where $X =$ c.cs. of N/10 NaOH used.

One c.c. of N/10 NaOH $= 0.0062$ grm. of boric acid.

The above is based on Richmond's method of estimating boric acid.

FLUORIDES (Hehner's method).—One hundred grm. of the sample are melted in a beaker and kept warm till the aqueous layer settles. The contents of the beaker are poured into a separating funnel, the beaker being washed out with two lots of 25 c.c. of petroleum ether and then with two lots of 5 c.c. each of water. The contents of the funnel are allowed to settle out and the aqueous layer run out into a platinum basin and rendered slightly alkaline with sodium carbonate, evaporated to dryness, and ignited till nearly white. The residue is taken up with water, and, without filtering, an excess of 20 per cent. solution of $CaCl_2$ added (this will be about 20 c.c.) ; the mixture is brought to the boil and an excess of

Na_2CO_3 (about 20 c.c. of a 20 per cent. solution) added.
The liquid is filtered (the filtrate being tested to see if the
precipitation be complete) and the filter and contents
dried and ignited in a platinum basin. To the residue
are added 30 c.c. of a 20 per cent. solution of acetic acid,
and the whole allowed to boil on a sand-bath for fifteen
minutes, covered with an inverted funnel. The contents
of the basin are then washed on to a small filter with hot
acetic acid solution, and the filter dried and ignited in
a platinum crucible and weighed. The residue is mixed
with a few drops of pure concentrated H_2SO_4, and the
crucible covered with a waxed watch-glass on which some
design has been scratched with a pin. The watch-
glass is filled with water and the crucible heated on a
hot plate or the top of a water bath for thirty minutes.
The glass is then removed and examined for etching.
If fluorides are indicated the crucible is then ignited
very cautiously in an inclined position and re-weighed.
The fluorides having been converted into sulphates by
the operation, the amount present may be approximately
calculated, since 78 parts of CaF_2 give 136 parts of
$CaSO_4$. It is here assumed that all the residue is
calcium sulphate derived from calcium fluoride, and in
the case of butter this is practically correct. In very
exact work a blank experiment with pure butter should
be done and the small quantity of residue subtracted
from the weight of $CaSO_4$ found in the test.

If boron compounds are known to be absent and an
indication of the presence of fluorides only be required,
the treatment with $CaCl_2$ and Na_2CO_3 may be omitted,
as, in this case, the test will not be vitiated by the
formation of volatile boro-fluorides.

BENZOATES AND SALICYLATES.—Fifty grm. are melted
(less if only salicylates are being looked for) and shaken
violently with 100 c.c. of water containing 1·0 per cent.

$NaHCO_3$, in a separating funnel, and allowed to separate. The milky aqueous layer is run off, made slightly acid with hydrochloric acid, and neutralised to litmus paper with a solution of sodium hydroxide and cleared by adding 10 c.c. of Fehling copper sulphate solution, followed by 10 c.c. of a solution of potassium hydroxide (containing 31·15 grm. per litre) and the mixture filtered. The filtrate is rendered acid with sulphuric acid and shaken out with 50 c.c. of ether. The aqueous layer is run off and the ether washed two or three times with a few cubic centimetres of water. It is then mixed with about 10 c.c. of water and one drop of phenolphthalein solution, and a saturated solution of barium hydrate run in until, on violently shaking, the pink colour remains permanent. The aqueous layer is then filtered into a small porcelain dish and evaporated to 1 or 2 c.c., and again filtered through a small filter into a test-tube. Very dilute acetic acid (1 100) is added drop by drop until the pink colour is discharged and then one or two drops of freshly prepared neutral solution of ferric chloride. In the presence of *salicylates* a *violet* colour will be produced, while in the case of *benzoates* a *flesh-coloured turbidity or precipitate* is formed.

When both salicylic and benzoic acid are present together the solution, instead of being a clear violet, is turbid. Herde and Jacob (Zeit. Untersuch. Nahr. Genussm., 1910, vol. xix, p. 137) state that salicylic acid can be destroyed in the presence of benzoic acid by means of potassium permanganate, but the authors have not been successful with the process.

Estimation of salicylic acid. —This will not often be required, and is rendered difficult on account of the solubility of the acid in fat.

About 10 grm. of the sample are boiled with 20 c.c. of alcohol three times, pouring off the alcohol

through a small filter after cooling sufficiently to solidify the fat. The alcoholic extract is diluted with 150 c.c. of water and neutralised with sodium hydroxide solution and 60 c.c. distilled off. To the residue are added 10 c.c. of N/sodium citrate (70 grm. of citric acid neutralised with NaOH and made up to 1000 c.c.) and then 10 c.c. basic lead acetate solution (p. 310), and then 10 c.c. of N/NaOH. Five c.c. of N/HCl are then added and 40 c.c. of a saturated solution of sodium chloride, the whole made up to 250 c.c. and filtered. The salicylic acid is extracted from 200 c.c. of this filtrate by acidification with sulphuric acid and shaking out with ether. The ether is extracted by placing it in a separator with 20 c.c. of water and one drop of phenolphthalein solution and running in N/10 NaOH till the aqueous layer is permanently pink. This is run off and the ether washed with two more quantities of 20 c.c. of water and the water extract made up 100 c.c. In this solution the salicylic acid is easily and accurately determined colourimetrically in Nessler glasses against a standard solution of salicylic acid (0·01 grm. per litre) using a solution of ammonia iron alum. The salicylic acid test solution should be diluted till the colour with the iron alum solution is easily compared with that of the standard. The iron alum solution is made by dissolving 1 grm. in 500 c.c. of water and boiling down to 100 c.c. and filtering before use. Two c.c. are added to 50 c.c. of the salicylic acid solutions in a Nessler glass.

The above method is a modification of methods of Fellenberg, Harry, Mummery, Revis and Payne.

COLOURING MATTERS—The following tests will usually be sufficient to detect such colours as are generally used in butter and margarine. If a more elaborate investigation be required, the method of Leeds (Analyst, 1887, vol. xxii, p. 150), or the still more elaborate

methods of Rota, should be employed (Chem. Zeit., 1898, p. 437).

ANNATTO.—A few grammes of the clear filtered fat are shaken with about 5 c.c. of warm dilute (10 per cent.) sodium hydroxide solution. The mixture is poured on to a wet filter and kept warm, till the greater part of the water has run through. The melted fat is then poured off the filter-paper, which is gently washed with cold water. In the presence of annatto, the paper will be stained a *reddish-yellow* of an intensity dependent on the quantity of annatto present. If the stain be very slight or indefinite, the paper should be dried and moistened with one drop of a 5 per cent. solution of citric acid, when in presence of traces of annatto a distinct *pink* colour will be produced, even when there is not sufficient annatto to produce a definite yellow stain on the paper.

AZO-DYES (Doolittle's method).—About 2 grm. of the filtered fat are placed in each of two test-tubes together with 5 c.c. of petroleum ether to prevent solidification of the fat. To one test-tube is added 1 c.c. of dilute (1 : 3) hydrochloric acid, and to the other 1 c.c. of dilute (10 per cent.) potassium hydroxide, the tubes being thoroughly shaken and allowed to stand. If an *azo-dye* be present, the lower layer in the hydrochloric acid tube will be *pink*, while that in the potash tube will remain *colourless*. In the case of annatto, the acid layer will remain colourless, while the alkaline layer (or, as more often happens, an intermediate layer of precipitated soap between the fat and alkaline layers) will be coloured a bright yellow. As a great number of mixtures of annatto and azo-dyes are sold for colouring purposes (and often as genuine annatto), both reactions will often be found to occur. Certain azo-dyes do not give satisfactory results with Doolittle's method

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in the presence of water, and in this case *Low's method* should be employed :

For this purpose about 1 c.c. of the melted fat is mixed with 1 c.c. of a mixture of 1 part of concentrated sulphuric acid and four parts of glacial acetic acid, and the mixture heated nearly to boiling with constant shaking. In the presence of *azo-dye* the acid solution on settling out will be coloured *pink or reddish,* practically no colour being produced in their absence. The colour often appears before heating.

Examination of the Fat.

A sufficient quantity of the sample is melted in a beaker at about 60° to 70° C., and kept warm until the bulk of the water and curd have settled out. The liquid fat is then decanted through a plaited filter-paper, of a thick soft variety (C. S. and S., No. 604), preferably in a hot-water funnel, as no partial solidification of the fat must be allowed during filtration.

The fat is received into a clean dry bottle, and should be quite clear and bright, and, if considered necessary, a few pellets of dry filter-paper may be dropped into the fat to absorb any traces of water which may be present.

Butter=Fat.

The examination is usually made for the presence of margarine fats. Coconut oil is probably seldom added *per se,* but on account of the use of large quantities of this fat, as well as of palm kernel oil, in many modern margarines, these might easily occur. On account of the wide variations in the figures obtained for pure butter-fat, the greater number of tests are of little or no value by themselves, and have only a cumulative significance. It is necessary, therefore, to employ those

tests which will yield the most valuable information. After careful consideration the authors are of the opinion that the indications derived from the determination of the *Reichert-Meissl-Polenske-Kirschner* figures and of the *baryta value* by the method of Avé Lallement, supported by a few qualitative tests, will give all the information with regard to adulteration which analytical methods are capable of. It must, however, be remembered that adulteration with animal fats produces butters which are similar in their composition to those which are produced naturally by cows kept under abnormal conditions, or suffering from functional disorders of the udder. It is of importance, therefore, when coming to a decision with regard to butters which appear to be adulterated with small quantities of animal fats, to obtain, wherever possible, all the information available regarding the history of the sample, as the authors themselves do not hold the opinion that the abnormal should always be labelled as adulterated, or that the food value of a butter is dependent on its Reichert-Meissl value. If definite indications of the presence of coconut oil are found, it may be taken as practically certain that the sample is adulterated. The recent work of some investigators certainly shows that special types of feeding, particularly with coconut oil cake, may lead to abnormally high Polenske values, but it seems hardly probable that this practice is likely to afford much difficulty in ordinary work.

Of the two main processes here given for the examination of butter-fat, the Reichert-Meissl-Polenske-Kirschner process is based on the fact that butter-fat is unique in containing glycerides, into whose composition butyric and caproic acids enter. It is these acids which account for nearly the whole of the Reichert-Meissl value, while the Kirschner value is dependent

almost exclusively on the butyric acid present, the caproic acid exerting but small effect, on account of the insolubility of silver caproate. The Polenske value is governed almost entirely by the presence of glycerides containing caprylic, capric and lauric acids, though, in practice, such acids as myristic and palmitic play a small part. It is for this reason that butter-fat, containing as it does but small quantities of glycerides having these water-insoluble-volatile acids, shows but a small Polenske value relative to the Reichert-Meissl value, while coconut products, which are largely made up of them, give a very high Polenske value. The addition of them to butter-fat, therefore, depresses the Reichert-Meissl value somewhat and decidedly raises the Polenske value.

The process of Avé Lallement, depending as it does on the relative solubility of the barium salts of the fatty acids present, covers, indeed, much the same ground as the last process, but to the authors it has this advantage, viz. that whereas a considerable quantity of lard or margarine mixture (not containing coconut products), may be added to butters without transgressing the arbitrary limit of 24 for the Reichert-Meissl value, the transition from a negative to a positive value in the formula $b-(200+c)$ of the Avé Lallement process takes place much more rapidly, and will often point to the addition of such mixtures when the evidence from the Reichert-Meissl value is not sufficient. Further, the inclusion of coconut products in the margarine mixture does not alter the evidential value of the formula $b-(200+c)$, in sharp contra-distinction to the balancing effect which may be obtained for most of the values for butter when lard and coconut products are added together.

Reichert-Meissl-Polenske-Kirschner Method.

Five grm. of the fat and 20 grm. of glycerine are weighed into a 300 c.c. flask, and 2 c.c. of a solution of sodium hydroxide (made by dissolving stick caustic soda in an equal weight of water) added. The flask is heated over a flame, with constant shaking, till it clears suddenly. The flask is allowed to cool somewhat and 100 c.c. of recently well-boiled, distilled water added, and solution of the soap effected. 0·1 grm. of powdered pumice (which has been sifted through butter muslin, as the grade and quality are important) is added, and then 40 c.c. of sulphuric acid solution (60 grm. of concentrated sulphuric acid diluted to 1000 c.c. and the solution adjusted so that 35 c.c. neutralise 2 c.c. of the above sodium hydroxide solution). The flask is *at once* connected with the condenser and heated over a small flame till the insoluble acids are *completely* melted ; the flame is then increased and 110 c.c. distilled in nineteen to twenty-one minutes. Condenser water should be from 18–20° C. and dimensions of apparatus exactly as given by Polenske (see Fig. 5). When 110 c.c. have distilled, the flame is removed and a 25 c.c. cylinder placed under the condenser to catch any drops. The 110 c.c. flask and contents are stood in water at 10°–15° C. for fifteen minutes. The contents of the 110 c.c. flask are then filtered and 100 c.c. titrated with N/10 *baryta*, using 0·1 c.c. of a 1 per cent. solution of phenolphthalein as indicator. This number of c.c. increased by one tenth, after subtraction of the blank (which must be determined in an exactly similar way, by using all the reagents except the fat)[1] is the *Reichert-*

[1] In carrying out the blank test, the greatest care should be exercised not to overheat the glycerol soda mixture ; the solution after heating should be quite colourless.

Fig. 5.

Meissl value. The condenser, cylinder and 110 c.c. receiver are washed with 18 c.c. of cold water, which are then poured over the filter used to filter the distillate, and rejected. The condenser is washed out with four successive portions of 10 c.c. of neutral alcohol, which are received in the cylinder and poured over the filter into the 110 c.c. flask, the mixed alcohol solutions being then titrated with N/10 baryta or soda, using phenolphthalein as an indicator. A blank value is obtained in a similar way. The number of c.c. of N/10 alkali used, less the number used for the blank, is the *Polenske value.*

Rather varying results have been obtained by various observers, but the following table will be found a very fair guide :

Reichert-Meissl values.					New butter values.
32	.	.		.	3·5
31	.				3·2
30			.		3·0
29	.		.	.	.	2·9
28			.	.	.	2·7
27	.		.	.	.	2·4
26	.			.	.	2·0
25	.	.		.	.	1·8
24	.	.	.	.	.	1·7
23	.	.			.	1·6

A " new butter value," exceeding by 0·5 c.c. the figure corresponding to the Reichert-Meissl value found, indicates the presence of coconut or palm kernel oil or their products.

As it seems that the Kirschner value (see below) is practically a measure of the butyric acid present in the sample, it is evident that there will be greater evidence

of adulteration with coconut oil if this figure be compared with the Polenske value. This point has not been sufficiently worked out yet, but the authors venture to suggest the following values :

Kirschner value.							Polenske value.
20	.	.	.	.	.	.	1·6
22	.	.	.	.	.	.	2·1
24	.	.	.	.	.	.	2·6
26	.	.	.	.	.	.	3·2

A variation of 1·0 must be allowed either way in the Polenske value corresponding to any particular Kirschner value, the addition of less than 5 per cent. of coconut oil causing the Polenske value to fall outside this limit.

Kirschner's Extension of the above Method.

To the 100 c.c. of the 110 c.c. distilled and titrated with baryta (care having been taken not to exceed the neutral point) is added 0·5 grm. of finely powdered silver sulphate, and the whole allowed to stand for an hour with occasional shaking. The liquid is then filtered, 100 c.c. measured off, 35 c.c. of water and 10 c.c. of sulphuric acid (as previously employed) added, together with a long piece of aluminium wire, and 110 c.c. again distilled off in the standard Reichert-Polenske apparatus in twenty minutes ; of the distillate 100 c.c. are titrated with $N/10$ soda or baryta, and the number of c.c. used, corrected for the blank, is calculated to the Kirschner value by the following formula :

$$K = x \cdot \frac{121 \ (100 + y)}{10000}$$

where $x =$ the corrected Kirschner titration,

$y =$ the number of c.c. of the baryta solution used to neutralise 100 c.c. of the original R -M. distillate.

The Barium Method of Avé-Lallement.

Five grm. of the filtered fat are saponified with
50 c.c. of approximately N/2 alcoholic sodium hydroxide
(carefully standardised against N/2 HCl), boiling for
thirty minutes (see saponification value). While the
solution is still warm, it is titrated with N/2 hydro-
chloric acid to phenolphthalein. The alcohol is then
removed as completely as possible by boiling and
blowing air into the flask. The soap is dissolved in
hot, recently boiled, distilled water, and transferred
to a 250 c.c. flask, brought to a temperature of 40° C.,
and made up to the mark at that temperature. One
hundred c.c. are pipetted off into a flask, which is stood
in a boiling water bath for five minutes, and then
50 c.c. of approximately N/5 barium chloride solution
(about 25 grm. of crystallised $BaCl_2.2H_2O$ in 1000 c.c.)
are added. The mixture is allowed to remain for
fifteen minutes in the water bath, to cause the insoluble
barium salts to coalesce. The contents of the flask are
cooled and filtered into a 250 c.c. flask, washing the
insoluble soaps well, and making up to the mark.
Two hundred c.c. are pipetted into a beaker, acidified
with 1 c.c. of concentrated HCl, heated on a sand-
bath nearly to boiling, and 10 c.c. of approximately N/1
sulphuric acid then run in. The beaker is allowed to
stand overnight, and the precipitate filtered on a Gooch
crucible, and washed till free from chlorides, and finally
with two quantities of 10 c.c. of warm alcohol. It is
then dried to constant weight. The weight of barium
sulphate found is increased by 25 per cent., and calcu-
lated to BaO ($BaSO_4 \times 0.657 =$ barium oxide). This
is subtracted from the barium oxide value of the
barium chloride solution (which must be standardised

in an exactly similar way). The result is the barium oxide value of the acids forming insoluble salts from 2 grm. of fat, and this, calculated to 1 grm. of the fat, = *insoluble barium oxide value* (*b*). The saponification value, also calculated to barium oxide (KOH × 1·367 = barium oxide) for 1 grm. of fat = *total barium oxide value* (*a*), and *a* − *b* = *soluble barium oxide value* (*c*), from which is calculated the value of *b* − (200 + *c*.).

Butter-fat practically always gives a negative value for this formula, while both margarine and coconut products give a high positive value. The sufficient addition of these therefore, causes the value of the formula to become positive (see tables, pp. 126–127). In the case of the addition of coconut products, the insoluble barium oxide value is usually *above* 260.

The method gives evidence of the presence of either coconut oil or lard compounds, the effect of the presence of these together being additive and not mutually destructive as in many other forms of investigation.

The actual mean molecular weights are easily determined by the use of the following formulæ :

b = Insoluble baryta value.

c = Soluble baryta value.

K = Saponification value.

U = Unsaponifiable matter.

M_o = Mean molecular weight of fatty acids forming insoluble barium salts.

M_1 = Mean molecular weight of fatty acids forming soluble barium salts.

$$\left.\begin{array}{l} S \\ S_o \\ S_1 \end{array}\right\} \text{ weight of} \left\{\begin{array}{l} \text{total fatty acids.} \\ \text{acids forming insoluble barium salts.} \\ \text{acids forming soluble barium salts.} \end{array}\right.$$

$$S_o = \frac{M_o \times b.}{76 \cdot 7} \div 1000$$

$$S = 1 - (K \times 0.0002258 + U)$$
$$S_1 = S - S_0$$
$$M_1 = \frac{S_1 \times 76.7}{c.} \times 1000.$$

S_0 is directly estimated by drying and weighing the insoluble barium soaps and igniting.

_____

If the foregoing methods give indication of adulteration (see tables), it may then become desirable to make such other determinations as the refractive index, iodine value, etc., in order to determine as closely as possible the amount of the added substances.

It is also recommended to apply the following tests:

The Valenta Test.

The addition of lard and other animal fats causes the turbidity temperature of a solution of the glycerides in acetic acid to be raised, while that of coconut and palm kernel oils lowers the turbidity temperature. The turbidity temperature in the case of pure butter-fats unfortunately varies considerably, but the test, if intelligently performed and with due consideration of its limitations, is often of great help. The personal equation is a large factor in the results obtained, and determinations should be made with some pure butters by anyone using the test. The following is a simple and efficient method of carrying out the test:

A long thin test-tube, preferably of Jena glass, about 0.5 in. in diameter, and sufficiently long to take in the scale of a thermometer up to $60° C.$, is marked accurately at 3 and 6 c.c. with lines all round the tube. A thermometer with very small bulb is fixed in the tube by means of a cork, so that the bulb is opposite the 3 c.c. line. The carefully dried butter-fat (filter-

paper pellets should be shaken up with it beforehand) is measured in at 27° to 29° C. till the bottom of the meniscus coincides with the 3 c.c. line. Absolute acetic acid (Kahlbaum's is to be preferred) is then run in until the 6 c.c. line is reached (the acid should be measured at a definite temperature, say 15 to 16° C.). The thermometer is inserted and the fat dissolved by shaking in water at about 50° C. The tube is then withdrawn from the water and the contents allowed to cool in the air, shaking gently, and holding the tube in a good light. Immediately the faintest turbidity is noticed the temperature is read. The tube is then slightly warmed and a fresh reading obtained. The end point is quite sharp, and consecutive readings should scarcely differ.

The authors obtain figures usually lying between 30° and 42° C. for pure butters, though they find low numbers prevailing during the early months of the year. Ten per cent. of lard produces a rise of about 7° C.

The Halphen Test (see p. 52).

As cotton-seed oil is never a constituent of pure butter, a positive result may be taken as absolute indication of adulteration, in spite of the fact that cows fed on quantities of cotton-seed oil cake are said to produce butters giving positive results. At the present moment it may be taken that about 80 per cent. of the margarines in this country contain more or less cotton-seed oil. If present, a quantitative idea may be obtained by comparison.

Baudouin's Test (see p. 54).

As nearly all margarines made for sale on the continent have to contain sesamé oil, this test is of some

significance. Care must be taken to do a blank, using
no furfural, as if aniline colours be present a pink
colour will be produced in the absence of sesamé oil.
If a colour be obtained in both blank and test, the
test will be a deeper colour if sesamé oil be present.

Phytosteryl Acetate Test (see p. 44).

In exceptional cases in which the addition of a
vegetable oil is suspected, but of which more definite
evidence is required, this test becomes a final court
of appeal.

Microscopical Appearance of the Fat.

The appearance of thin films of butter under pola-
rised light affords some evidence of the addition of
fats which have, in the course of their manufacture,
been melted and re-set. When genuine butter is
examined under a low power ($\frac{1}{2}$ in.) in a very thin
film, made by pressing out a speck of the butter
between a glass slide and cover slip, between crossed
Nicols, the field appears uniformly dark. Light
patches on the dark field point to the presence of
margarine fat or renovated butter (*i. e.* butters which
have been melted, washed with water and re-churned
with milk). The results of this test must be inter-
preted with care as crystals of salt may be mistaken
for crystals of fat. The examination is rendered
easier if a cardboard tube be placed between the pre-
paration and the microscope tube so as to enclose the
objective.

The Foam Test.

Genuine butters when heated in a spoon over a small
flame boil quietly with a gentle hissing, and with the

production of considerable foam, while renovated butters crackle considerably with much spluttering and little foam. The results of this test may be conveniently noted when determining the water by Patrick's method.

Interpretation of Results.

The following table gives a number of results for various pure butters using the above mentioned tests :

Butter.	R-M.	Pol.	K.	Sap. V.	Total Ba.	Insol. Ba.	Sol. Ba.	Diff.
Danish	30·01	2·15	23·57	228·3	312·0	253·4	58·6	− 5·2
,,	30·58	2·52	23·0	228·7	312·6	249·0	63·6	−14·6
,,	30·59	2·67	23·79	225·7	308·6	251·2	57·4	− 6·2
,,	29·71	2·68	24·18	231·1	315·9	252·9	62·9	−10·0
,,	31·22	2·64	24·26	230·2	314·7	255·7	58·9	− 3·2
,,	30·23	2·09	21·31	227·9	311·5	252·9	58·7	− 5·8
New Zealand	33·13	3·16	24·35	231·7	316·7	250·4	66·5	−16·1
,,	33·51	2·35	27·57	229·3	313·4	244·7	68·7	−24·0
,,	30·83	2·15	25·63	228·0	311·6	253·9	57·7	− 3·8
,,	30·93	1·81	23·17	224·0	305·8	249·1	56·7	− 7·6
,,	32·65	2·92	24·20	232·1	317·2	251·6	65·6	−14·0
English	29·79	2·44	21·94	228·7	312·7	253·0	59·7	− 6·7
,,	30·49	2·59	23·71	228·7	312·6	253·8	58·8	− 5·0
,,	28·74	2·57	21·76	229·1	313·2	250·6	62·6	−12·0
,,	32·23	2·99	22·04	232·0	317·1	254·5	62·6	− 8·1
French	29·88	2·65	21·59	228·0	311·6	252·4	59·3	− 6·9
,,	26·88	2·42	23·76	228·0	311·6	252·7	59·0	− 6·3
,,	28·84	2·42	23·17	226·2	309·2	253·2	56·0	− 2·8
,,	31·49	3·08	22·01	231·5	316·4	251·7	64·7	−13·0

The methods of examination given above do not furnish indications of the actual amount of adulteration. The following figures will give some indication of the type of result obtained with mixtures of pure butter and coconut oil when using the Reichert-Meissl-Polenske-Kirschner method and the method of Avé Lallement.

	Val-enta.	Iod. No.	R.-M. val.	Pol. val.	Sap. val.	Total Ba. (a)	Insol. Ba. (b)	Sol. Ba. (c)	b − (200 + c).
Butter A	28·8	33·9	28·7	3·2	228·4	312·2	255·4	56·8	− 1·4
Butter A + 10 °/₀ coconut oil	25·2	31·4	26·6	4·1	231·1	315·9	262·8	53·1	+ 9·7
Butter B	30·3	36·5	28·1	2·5	227·8	311·4	254·8	56·6	− 1·8
Butter B + 10 °/₀ coconut oil	26·4	33·7	25·8	3·9	230·3	314·8	260·5	54·3	+ 6·2
Butter C	27·0	35·7	30·5	3·5	227·0	310·3	255·1	55·2	− 0·1
Butter C + 10 °/₀ coconut oil	24·0	32·8	28·0	4·3	230·5	315·1	263·6	51·5	+ 12·1

The mutual interdependence of the constants of butter-fat is well illustrated by the following table due to Thorpe (Journ. Chem. Soc., 1904, vol. lxxiii, p. 254).

No. of samples.	Reichert-Meissl number.	Sp. gr. 37·8° / 37·8°	Saponifi-cation value.[1]	Zeiss butyro-refracto-meter number at 40°.[2]	Soluble[3] acids per cent. on fat.	Insoluble acids per cent. on fat.	Mean molecular weight of insoluble acids.
7	22·5	0·9101	219·65	44·7	4·3	90·1	266·9
17	23·5	0·9104	221·39	44·2	4·5	89·7	265·5
15	24·5	0·9108	223·24	44·2	4·7	89·4	265·0
27	25·5	0·9110	223·41	44·0	4·8	89·3	264·2
37	26·5	0·9113	225·39	43·7	4·9	88·9	261·9
51	27·5	0·9114	226·75	43·3	5·2	88·7	261·7
78	28·8	0·9118	228·32	42·8	5·4	88·4	260·9
56	29·5	0·9120	229·91	42·8	5·6	88·3	259·6
41	30·5	0·9123	231·43	42·6	5·8	87·9	260·1
18	31·3	0·9125	232·30	42·4	5·7	87·9	258·0
10	32·6	0·9130	232·58	42·1	6·0	87·7	257·8
357							

[1] Calculated by Lewkowitsch from the saponification equivalents given by Thorpe. [2] Calculated from 45°C. by the authors. [3] Calculated as butyric acid.

Reference to these figures will often be of help in detecting adulteration.

Gross adulteration with lard products or margarine containing coconut or palm kernel oils with or without other vegetable or animal fats will be easily detected as already stated by the methods given. When, however, the addition is very small (say 10 per cent.) and is composed of oils and fats other than coconut or palm kernel products, the effective detection is decidedly difficult, unless some oil giving a characteristic qualitative test has been introduced. As already stated, in deciding the quantity of any such addition all possible values should be employed and the mean of their indications returned.

For public health control purposes in England a Reichert-Meissl value of 24 is taken to be the lowest limit for pure butter, but with the occurrence of butters obtained principally from Australia and New Zealand, having Reichert-Meissl values of 30 and over, the opportunity for the addition of animal fats is great, and will be passed over if reliance be placed on the Reichert-Meissl value alone. Such a case is exemplified by the following figures :

	Butter.	Same butter + 10 per cent. lard.
Valenta	30·2	35·2
Iodine value	38·7 per cent.	40·6 per cent.
R.-M. value	30·8	27·7
Pol. value	2·9	2·4
Kirschner	21·9	19·5
Sap. val.	224·8	221·8
Total Ba.	307·3	303·2
Insol. Ba. (b)	252·8	254·6
Sol. Ba. (c)	54·5	48·6
$b - (200 + c)$	$-1·7$	$+6·0$

Iodine Value.

The iodine value may be used in certain cases for confirmatory purposes, but the variations in genuine butter are so wide that, in itself, it furnishes no evidence at all of adulteration. The authors have found the following to be fairly mean values :

Danish butters	.	.	38 (Wijs)
French ,,	.	.	37 ,,
Irish ,,	.	.	42 ,,

The variations lie between 33 and 45. As the addition of 10 per cent. coconut oil lowers the figure about 3, and 3 per cent. of lard only raises the figure about 9, little evidence is given by the iodine value.

Margarine Fat.

As the composition of margarine fat may be of a most complex nature, it will be necessary to make every determination which is likely to throw light on the composition (see p. 75 *et seq.*).

The saponification value (p. 21) is first determined as yielding the most useful information and guidance. If the value be below 193, the rape oil group or unsaponifiable matter are indicated and should be looked for (see " Unsaponifiable Matter," p. 48 ; " Hexabromide Test," p. 42, and " Tortelli and Fortini's method," p. 38).

If the value be above 200, the presence of coconut, palm kernel, cohune oil or butter-fat may be tentatively inferred.

The determination of the *Reichert-Meissl-Polenske-Kirschner values** will show whether any such fats are actually present, and in particular, *whether there is any butter-fat.* The test having been carried out, reference
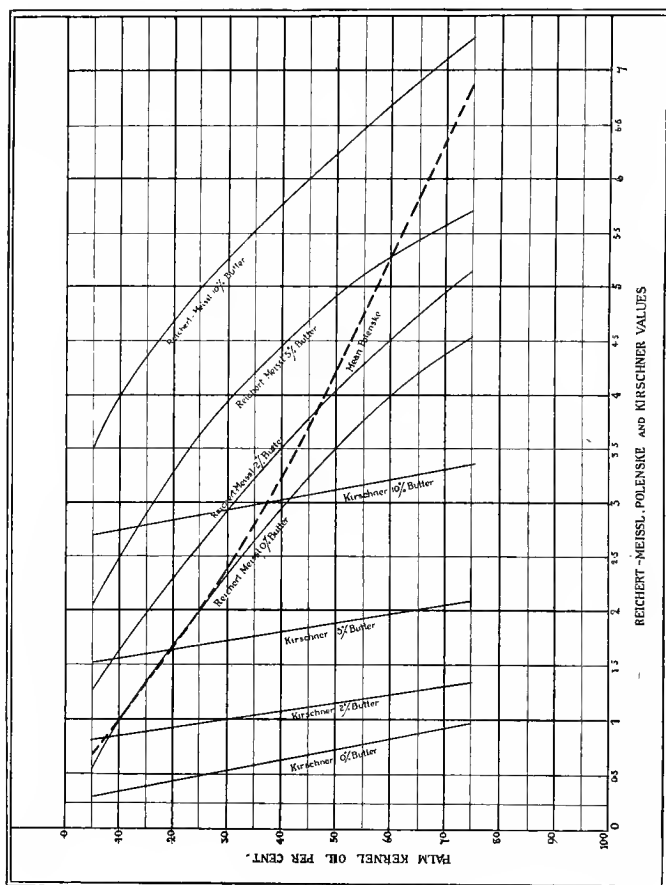
* See Appendix A.

Fig. 6.

should be made to the following tables and curves,
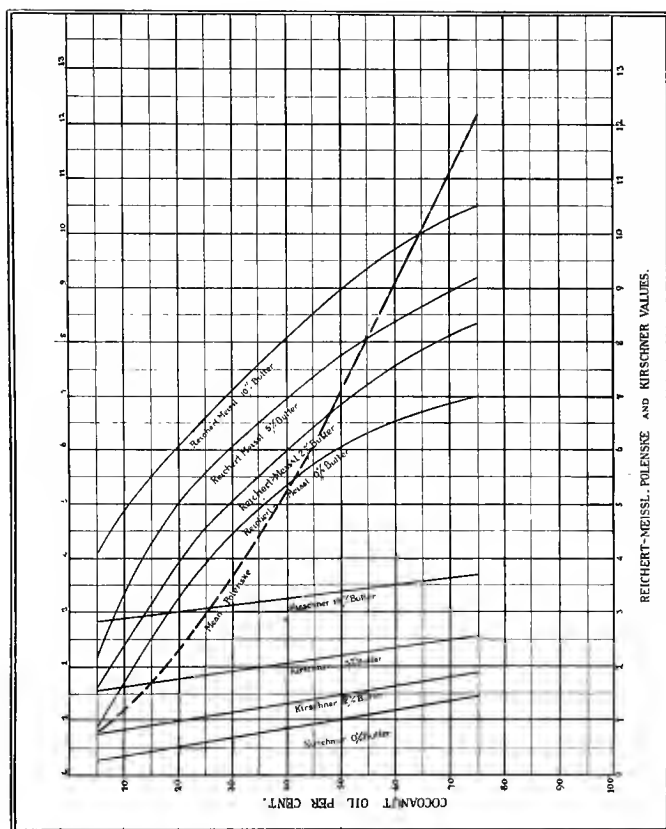which have been compiled from determinations made

FIG. 7.

by the authors using the standard process described on
p. 117, and published in the Analyst, 1912, vol. xxxvii,
p. 183.

Coconut oil		Polenske indicator value.		Butter-fat.			
				0 per cent.	2 per cent.	5 per cent.	10 per cent.
0 per cent.		0·45	K.	0 18	0·80	1·49	2·70
			R.-M.	0·38	0·92	1·70	3·25
5	,,	0·76	K.	0·25	0·75	1·55	2·82
			R.-M.	0 87	1·65	2·15	4·10
10	,,	1·22	K.	0 34	0·84	1·60	2·90
			R -M.	1·60	2·45	3·42	4·90
15	,,	1 75	K	0·42	0·92	1·68	2·96
			R.-M.	2·52	3·15	4·35	5 55
25	,,	2·91	K.	0·60	1·08	1·82	3·08
			R.-M.	3·92	4·57	5·55	6·55
50	,,	7·10	K.	1·02	1·50	2·20	3·38
			R.-M.	6·05	6·88	7·72	8·95
75	,,	12·19	K.	1·45	1·92	2·55	3·70
			R.-M.	7·00	8·35	9·20	10·50
100	,,	16·50	K.	1·88	—	—	—
			R.-M.	8·08	—	—	—

Palm kernel oil.		Polenske indicator value.		Butter-fat.			
				0 per cent.	2 per cent.	5 per cent.	10 per cent.
0 per cent.		0·31	K.	0·18	0·80	1·49	2 70
			R.-M.	0·38	0·92	1·70	3·25
5	,,	0·59	K.	0·30	0·80	1·51	2·70
			R.-M.	0·53	1 27	2·05	3 50
10	,,	0·93	K.	0·35	0·85	1 54	2·75
			R.-M.	1·00	1·62	2 50	4·00
15	,,	1·30	K.	0·40	0 90	1·57	2·80
			R.-M.	1 35	2·00	2·90	4·35
25	,,	1·67	K.	0·48	0·97	1·65	2·87
			R.-M.	1·97	2 60	3·62	4·97
50	,,	3 98	K.	0·72	1·16	1·87	3 12
			R.-M.	3·50	40·5	4·92	6·22
75	,,	6·70	K.	0·97	1·35	2·07	3·35
			R.-M.	4 55	5·15	5·70	7·30
100	,,	9·82	K.	1·07	—	—	—
			R.-M.	5·22	—	—	—

In using these tables and curves the Polenske value is first noted, as this acts as an "indicator," showing among which figures the R.-M. and Kirschner values are to be sought. The Kirschner value then determines the presence (and probable percentage) or absence of butter-fat. The approximate agreement of the Reichert-Meissl figure with these indications determines the composition of the mixture. Of these three values (within the limits given) the Polenske value is practically independent of the presence of butter-fat. The values of the Reichert-Meissl and Kirschner figures vary, however, with the composition of the butter-fat used, though the variations are not wide. For instance, 10 per cent of butter in a margarine gave a Kirschner value of $1\cdot5$ for a butter of R.-M. value $= 23\cdot5$, and a Kirschner value of $2\cdot7$ for a butter of R.-M. value $= 30\cdot0$. The R.-M. value varied similarly with the Kirschner value, the corresponding values in the above case being $2\cdot25$ and $3\cdot25$. The mean Kirschner and R.-M. values given in these tables and curves correspond to a butter giving an R.-M. of $30\cdot0$. In the presence of coconut and palm kernel oils there is a distinct difference in appearance of the insoluble acids which float on the surface of the R.-M. distillate *when cooled in water at* $10^\circ C$. When palm kernel oil only is present the acids are white, hard and almost crystalline, while in the case of coconut oil they are nearly always partially oily.

The values obtained in this process are *practically independent* of the constituents of a margarine mixture, other than coconut and palm kernel products and butter-fat. In this lies the great value of the process, as it furnishes quantitative results which are a definite measure of a definite constituent; whereas in the case of all other values, such as the saponification,

iodine values, etc., the contributory effect of *each* con-
stituent has to be considered.

The values for the various mixtures given in the
foregoing tables were obtained by the use of the
whole oils. In practice, not only the whole oils, but
the " stearines " either alone or in conjunction, may be
employed. It therefore follows that figures will be
sometimes obtained which do not fit exactly into the
tables given. In such cases the percentage of these
products is not so definite and has to be tentatively
held and considered in conjunction with other analy-
tical values. If the " stearines " are suspected the
values of these, as given on pages 152 and 155, must
also be taken into account.

Cohune oil, which may soon be largely employed,
behaves like coconut oil.

Beef and lard fats should now be sought for by *micro-
scopical examination* of the deposit from ethereal solution
of the sample (pp. 56–57) (if necessary cooling to $0°$ C.),
bearing in mind that *oleo oil, having a low " stearine"
content, only gives deposits in concentrated solution, and
with great difficulty in the presence of fats and oils con-
taining no " stearine," as these exert a solvent influence.*

After this the *refractometer number* should be deter-
mined. In general, a reading over 50 will indicate
the presence of a *liquid* vegetable oil.

From the refractometer number (which in most
margarines will lie between 35 and 60) an idea will be
obtained of the weight of fat necessary to determine
the *iodine value*. For instance, if the refractometer
number be 35, use 1·5 grm., if it be 60 use 0·1 grm., and
for intermediate figures corresponding intermediate
weights (the above quantities suppose that 10 c.c. of
Wijs' solution is being employed). In the case of very
low iodine values it is of course unnecessary to look

for liquid oils.   The iodine value having indicated liquid vegetable oils the presence of cotton-seed oil is sought by *Halphen's reaction*, and in the case of a positive result the percentage is ascertained by comparison with standards as described under that test.

The presence of sesamé oil is similarly sought by *Baudouin's reaction*, taking the same precaution against the presence of aniline colouring matters as noted under " Butter-fat," and on page 54.

A consideration of the above results will usually give considerable information as to the composition of the fat under examination, for which purpose see the typical examples given on page 81 *et seq.*

When definite indications of the presence of certain oils and fats has been obtained it may be fairly taken that they are actually present.   There will, however, always be a considerable number of vegetable oils which yield no distinctive individual characteristics, but whose presence is evident from their general properties.

To definitely state that such and such an oil is present in these cases is often beyond the power of the most experienced oil analyst.   We can only refer the reader to the properties of the oils themselves and to careful attention to the behaviour of the fat under examination, as in many cases a clue can be obtained by little indications which are too many and too varied to enter into here.

It may in certain cases be necessary to add to the above determinations that of the *unsaponifiable matter*, this being, at the present time, practically the only analytical *clue* (not proof) to the presence of solid vegetable fats which simulate lard and beef, such as shea nut oil, and certain fats of the " Illipé " group, some of which are distinguished by an abnormally high amount of unsaponifiable matter, to which reference

will be made under their respective headings. The phytosteryl acetate test also may be a final court of appeal when small quantities of vegetable fats are mixed with animal fats, or *vice-versâ*.

In dealing with an oil for use in margarine manufacture without any knowledge of its source, the determination of the presence or absence of optical activity should never be omitted, as the possession of optical activity is a distinctive feature of the Chaulmugra group of fats, which are very poisonous.

Fats used in Margarine Manufacture.

It may be said, almost without contradiction, that at the present day there is scarcely an animal or vegetable fat (which can be procured in sufficient quantity) that has not been tried, or actually used in margarine, and even fish oils are being pressed into the service of the manufacturer. The consequence of this unfortunate idea that any oil or fat, if sufficiently refined, is suitable for the purpose has led on occasion to the use of consignments of oils having poisonous properties, with disastrous results. It is, therefore, necessary when giving an opinion on any unknown oil to make quite sure that it does not belong to such a poisonous group. Modern processes of refinement and deodourisation have made it possible to render nearly every oil both odourless and tasteless, although certain oils are liable to regain some proportion of their original taste with too great a rapidity to allow of their general use. As the variety of vegetable oils which are placed on the market is increasing daily, and in a most erratic manner, the examination of margarine mixtures is of a correspondingly variable nature. Consignments of fats are sold and used, and may perhaps never come again on the

market, and what is more disconcerting, an entirely different fat may often be sold under the same name as that of a previous consignment. For instance the name "Illipé butter" covers a large variety of solid vegetable fats of totally different composition, and the term is now practically void of any designative value.

Considerations, both climatic and financial, largely govern the use of fats by particular makers at particular times, and therefore a study of market prices and the magnitude of consignments may often save the analyst the trouble of seeking for a fat which he is unlikely to find, and also prove a useful guide to the fats most likely to be present.

The question of animal fats is particularly influenced by climatic conditions. For instance, margarine for summer trade must have a higher melting-point than that for winter use, the sale of margarine being quick on account of its liability to become rancid. In cold weather the manufacturer will be using less premier-jus and more oleo oil, so that the former is inclined to fall in price, while paradoxically the price of oleo oil increases, because concurrently with its production oleo-stearine appears as a bye-product, for which the margarine manufacturer has, at such a time, less use than for premier-jus. A large content of oleo oil is generally restricted to high-class margarines.

If, however, large quantities of suitable liquid vegetable oils are available, both oleo-stearine and premier-jus will be used in the production of cheaper margarines, as they provide the necessary stiffness.

Again, "price" almost entirely rules the question of neutral lard, which, although one of the commonest constituents of margarine, usually disappears when the price advances beyond a certain limit.

At the present time there is a growing tendency to

use vegetable substitutes for lard, and although a variety of these have been on the market for some time their use is now being reinforced by refined shea nut oil, and more particularly by shea nut " oleine." As vegetable lard substitutes, and, in fact, vegetable oils as a whole, are usually in a higher state of refinement than animal fats (particularly at level prices), this steady increase in the use of such fats is probably advantageous to the consumer.

Though cheaper than beef-fat as a rule, mutton-fat is seldom used in margarine on account of its peculiar flavour, and finds an outlet instead among cake and biscuit makers.

The great multiplicity of manufactured products obtained from oils, such as the commercial "oleines" and " stearines," and more recently the production of solid fats from liquid oils by " hydrogenization " processes,* render the interpretation of analytical figures very difficult, and unless very considerable every-day and up-to-date experience has been had, it is not advisable for the analyst to return definite percentages of any constituent of a margarine, or to go a step beyond that for which there are *absolutely definite analytical grounds.* It is better to give fairly wide limits for each constituent, and where the presence of vegetable oils is inferred, but for which no definite confirmatory test exists, to return all such simply as " liquid vegetable oils " without attempting a more elaborate differentiation.

Ghee (Ghi).

In eastern countries on account of the high temperatures which prevail, this stable form of butter-fat largely takes the place of ordinary butter, more

* See Appendix C.

especially for cooking purposes, etc. It is prepared by inoculating freshly boiled milk (usually of the buffalo) with sour milk, and after curdling has taken place, churning in a somewhat primitive manner. The fat so obtained is skimmed off, allowed to become somewhat rancid, and then heated in earthen pots until the water has evaporated. The fat clarifies on standing, and when sufficiently clear is run off from the sediment and constitutes " ghee " (see Analyst, 1910, vol. xxxv, p. 343, and 1911, vol. xxxvi, p. 392).

The analytical figures are in the case of pure samples practically those of ordinary butter-fat, but the Reichert-Meissl values may be very high on account of the use of buffalo milk for its preparation. Ghee, however, is seldom pure, and is much adulterated with both vegetable and animal fats. The *animal fat* is usually mutton fat, while the principal *vegetable adulterants* are phulwara butter and other Bassia fats, and less frequently liquid vegetable oils, such as arachis, cotton-seed, poppy-seed and sesamé oils, as well as coconut oil (which is liquid in such countries as produce ghee).

The examination of ghee follows the same lines as those for butter and margarine, and by means of the Kirschner value it is possible to absolutely certify the *absence of butter-fat* in " ghee substitutes."

The following table of figures gives a selection from analyses made by the authors (for reference see above) on pure and adulterated samples sold on the Eastern markets. It must be remembered that buffalo milk is chiefly used in the preparation of ghee, and that the fat of this milk seldom has a Reichert-Meissl value under 30, and may even approach 40.

Source. Price, per cwt.	Rangoon. 75s.	Rangoon. 57s.	Rangoon.* 40s.	Ambala. —	Ambala. —	Malabar coast. —	Bombay City. 1. —	Bombay City. 2. —	Bombay City. 3. —	Bombay City. 4. —
Reichert-Meissl value	30·58	18·04	0·44	29·3	31·5	24·4	25·70	26·20	28·40	29·80
Polenske value	1·62	1·33	0·47	2·6	1·66	1·8	0·90	1·5	1·60	1·40
Saponification value	228·8	213·9	193·4	223·8	229·1	228·2	213·8	223·6	224·9	225·4
Iodine value (Wijs)	30·63	40·85	55·73	30·92	29·6	—	37·28	29·24	28·11	29·55
Refractometer index at 40°C (Zeiss scale)	41·4	44·6	49·3	42·3	41·5	42·7	44·3	44·8	42·0	42·0
Specific gravity $\frac{99^\circ}{15}$	0·8632	0·8612	0·8577	0·8624	0·8631	—	0·8627	0·8619	0·8656	0·8656
Valenta No (°C.)	24	47½	95	33½	23½	—	43·5	42·5	36·0	33·5
†Baryta values: (a) Total	312·8	292·4	264·4	305·8	318·5	312·0	290·3	305·6	307·5	308·1
(b) Insoluble	251·7	255·7	263·3	254·9	248·7	256·7	256·8	256·2	252·4	251·5
(c) Soluble	61·1	36·7	1·1	50·9	64·8	55·3	35·5	49·4	55·1	56·6
$b - (200 + c)$	−9·4	+19·0	+62·2	+4·0	−16·1	+1·4	+21·3	+6·8	−2·7	−5·1
Free fatty acids (as oleic) per cent.	3·68	1·80	0·59	1·52	2·59	—	2·23	2·39	1·83	1·84
Solidifying point °C.	—	28	34	—	—	—	—	—	—	—
Unsaponifiable matter (per cent.)	—	—	0·43	—	—	—	—	—	—	—
Inferences	Pure.	Adulterated.	Milk fat entirely absent.	Slightly adulterated.	Pure.	Purity doubtful.	Highly adulterated.	Adulterated.	Pure.	Pure.

* Marked " Mixed with grease." † Avé Lallement's process (see p. 121).

CHAPTER V.

VEGETABLE OILS AND FATS.

THE vegetable oils and fats, derived from oil-bearing seeds and fruits, etc., are obtained, in nearly all cases, by the employment of pressure, usually hydraulic. For this purpose the material is coarsely ground and pressed *cold*, by which process the finest oil is obtained and the product is commercially known as "cold drawn."

The press cakes are then removed from the press, broken up and ground into a finer condition, heated in steam-jacketed kettles and again subjected to pressure while still *warm*. This second pressing produces an oil of slightly inferior quality, though, in some cases, there is no appreciable difference in quality between the products of the first and second pressings.

The high efficiency of some modern presses has, however, enabled the complete expression of all the *available* oil to be carried out in one operation, but when using them the material requires nearly always to be warmed before pressing. Recently the Anderson screw press has come into operation as a substitute for hydraulic machinery.

The press cakes derived from these processes usually contain from 5–10 per cent. of oil, according to the extent of pressure. Obviously the hard vegetable fats cannot be obtained by cold pressing, and must be heated both for first and second operations.

Another process, which, though by no means modern, has only of recent years become of practical importance, is that of extraction of the oleaginous material with volatile solvents—such as benzine, carbon bisulphide, carbon tetrachloride and trichlorethylene, etc. The earlier methods were not very efficient, chiefly on account of the impurity and unsuitability of the solvents employed, and also on account of the inefficiency of construction in the plant and of the difficulty of removing the solvent from both oil and meal. Modern extraction plants, however, have reached a high degree of efficiency in all these particulars, and considerable impetus has been given to the method by the introduction of *trichlorethylene* of great purity. This last point is one of great importance, as the insufficiently pure trichlorethylene, which was used at first, liberated small quantities of hydrochloric acid, which exerted a very deleterious action on the metal parts of the plant.

Extracted oils and meals are now found containing such slight traces of solvent that its presence cannot be detected in them and the extracted meals are suitable for feeding purposes. It should be understood that the word " extracted," when used in conjunction with an oil, is commercially applied to those obtained by extraction with solvent, no distinctive term being employed when " expressed " oils are referred to. An " expressed " oil should not therefore be spoken of as " extracted " by pressure. Sometimes the two processes are combined, the meal is first pressed and the press-cake broken up and extracted.

In many parts of the world, especially those localities in which oil-bearing plants grow and in which modern machinery has not been introduced, the native production of oils and fats is still carried out in a very primitive fashion, such as by the use of wedge presses

or more often by boiling and pounding the material with water, the oil being afterwards removed by skimming. Oils so prepared are usually characterised by a high percentage of free fatty acids, and possess a bad colour, strong taste and smell, and contain a considerable quantity of vegetable débris.

Many oils, when first expressed, are more or less deeply coloured with matter derived from the meal. This is particularly the case when " extraction " processes are used, and is very pronounced when trichlorethylene is the solvent. The colour can, however, be removed or greatly diminished, practically in every case, by one or other of the numerous bleaching processes now employed, filtration through animal charcoal being one of the most common. Alkali refining, though principally employed for the removal of free fatty acids, also effects considerable reduction in the colour.

The above details are, of course, common knowledge, and are all that the analyst needs to know. The details of modern oil refining are naturally trade secrets of the various manufacturers and the authors therefore cannot be expected to disclose any such, particularly as they do not come within the scope of this work.

It may not be commonly known that in oil mills, in which a variety of oils are produced, it would be much too costly a proceeding either to clean out the presses and tanks, etc., after each different batch of oil has been dealt with, or to have a separate plant for each particular variety of oleaginous material. It follows therefore necessarily that a certain admixture of a new batch with some of the preceding one will often take place, and this will account for the fact that traces of other oils are sometimes met with in samples which are commercially pure. From a commercial point of view

no objection can be taken to this so long as the real product is not depreciated thereby.

Products obtained from Vegetable Fats and Oils.

" Oleines " and " stearines."—Some of the liquid vegetable oils, on prolonged standing, deposit solid fat, more particularly in cold weather or when artificially cooled. This deposit is termed " stearine," though it need not, by any means, contain any glyceride of stearic acid. The clear oil is syphoned off and the " stearine " obtained by filter-pressing the residue. A particular example of this type of product is cotton-seed " stearine," which is largely used in soap manufacture and to a limited extent for margarine, and, in fact, this " stearine " is practically the only one of any considerable commercial importance obtained from liquid vegetable oils.

Oils from which the " stearine " has been separated during cold weather are commercially known as "winter oils," and, as they remain clear at all times, find a ready use as salad oils. The term " summer oil " is applied to those from which the " stearine " has been but incompletely separated.

In the case of solid vegetable fats, the " stearine " cannot be satisfactorily separated by any process of sedimentation at temperatures at which the oil is partially liquid. In such cases the fats are melted and allowed to " grain " (*i. e.* crystallise) by natural cooling. The solid mass is placed in bags and packed in layers between plates in a hydraulic press. The clear oil, which runs out on pressure, is known as the " oleine," while the hard residue left in the bags is, as in the case of animal fats, called the " stearine." While some of the softer fats may be pressed at ordinary temperatures,

some of the harder varieties require a temperature which will maintain them in a sufficiently plastic condition to enable "oleine" to be expressed. Analytically, the tendency in the case of " stearines " is towards a *lower* iodine value than that of the original oil, but the other values follow no definite course, except, as would be expected, the melting-point rises.

Foots.—This term is applied to any oleaginous sedimentary bye-product which is not *wholly fatty.* They may consist of soaps derived from alkali treatment, in which case they will include the alkali salts of the free fatty acids of the oil, together with neutral oil mechanically included, colouring matter, vegetable débris, free alkali and water, but the term is also applied to the vegetable débris obtained by sedimentation of the oil during the process of clarification.

*   *   *   *

In the following pages an attempt has been made to present the various vegetable oils and fats on a systematic plan. This has led to a somewhat stereotyped result, which, though satisfactory in the majority of cases, has been the cause of insufficient and unsuitable treatment in some instances, but it seemed that the advantages of tabulated presentation, both for ease of reference and for comparative purposes, outweighed these disadvantages.

Under the analytical figures given will be found only those which we consider to be of real use in practical work, and for the more elaborate experimental investigations which may be carried out, reference must be made to other works.

The column " Usual limits " is compiled from figures obtained by ourselves and by other investigators, omitting

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always any striking abnormalities, but giving sufficiently wide limits to include the greater number of samples.

The column "Typical specimen" is in the greater majority of cases based on our own figures.

Under the heading " Uses of non-fatty portion " we have given such analyses of meals and feeding-cakes, etc., as may be of interest. Except when otherwise stated, the figures are the results of our own analyses.

The classification here adopted is that devised by C. Ainsworth Mitchell in Allen's Organic Analysis, fourth edition, vol. ii. It is hardly necessary to say that only a selection from each group of oils is given here.

COCONUT OIL GROUP.

1. COCONUT OIL.*

2. PALM KERNEL OIL.

3. COHUNE OIL.

4. JAPAN TALLOW.

As some important manufacturers have recently decided to adopt the word "coconut" (in preference to "cocoanut") to designate the product obtained from *Cocos nucifera*, on account of the confusion which sometimes arises with the product of *Theobroma Cacao* (cocoa-butter), we have adopted this nomenclature.

Coconut Oil.

TRADE NAMES.—The refined oil, for edible purposes, is sold under various trade or proprietary names, of which the following are among the best known : Nucoline, Cocolardo, Vegetaline, Palmine, Nutrex, Nutto, vegetable lard, nut lard, etc.

SOURCE.—The fruit of *Cocos nucifera* (the ordinary coconut tree).

The husk of the nut is removed by hand. The nut is split in two and dried in the sun, preferably on sand, which takes about three days, the shell coming off on the first day. The " meat " so dried and removed is termed "copra." Large quantities are, however, dried in kilns, but the product fetches a lower price as the colour is darker unless special precautions are taken. The copra is usually shipped and pressed in Europe to avoid the loss of oil in transit by leakages and to save the expense of packing, and on account of the more efficient methods of pressing employed. About one fourth of the weight of the original nut (without fibre, but with shell and water) is " copra," which should not contain more than 5 per cent. of moisture.

CONTENT OF OIL (in copra).—63–70 per cent. On pressing 62–63 per cent. of oil and 37–38 per cent. of oil-cake are usually obtained from the average copra.

DESCRIPTION OF OIL.—*Appearance.*—White to yellowish fat, according to the quality of the copra and the method of preparation; when melted it forms a colourless to brownish-yellow oil.

Consistency.—Solid, greasy, somewhat crystalline fat, with a certain degree of brittleness, especially at low temperatures, but becomes soft and nearly liquid in summer (see " Melting-point ").

Taste and smell.—When unrefined, these may vary from the pleasant fresh taste and smell of coconut to strongly rancid and disagreeable. The best refined edible oils are absolutely odourless and tasteless.

POSSIBLE ADULTERANTS.—Actual adulteration is uncommon, palm kernel oil being the only likely adulterant, but an occasional form of sophistication is the removal of part of the " stearine," when the remainder is sold as " whole oil " ; such treatment lowers the setting point and raises the iodine valve.

LIABILITY TO RANCIDITY.—The best refined edible oils keep well, but the unrefined oil rapidly turns rancid, especially in the presence of moulds.

SPECIAL TESTS.—Distinguished by a high Reichert-Meissl value and very high Polenske value. Also by the highest saponification value of the commonly used fats (see palm kernel oil, manufactured products). The iodine value is low and the solubility in alcohol unusually great. Hinks (Analyst, 1907, vol. xxxii, p. 160) has taken advantage of this to separate a crystalline glyceride, which enables small quantities to be detected in butter by a microscopical examination of the alcoholic extract obtained under certain conditions.

USES OF THE OIL.—The refined " whole oil " is used to an enormous extent in every form of foodstuff to which a solid fat may require to be added ; probably no other vegetable fat is so extensively used, or adapted to so many purposes, and its use is daily increasing, as a constituent of margarine, cakes, biscuits, sweetmeats, etc.

MANUFACTURED PRODUCTS FROM THE OIL : THEIR USES.— " Oleines " and " stearines " are obtained by hydraulic pressure by methods described on p. 144.

The refined " stearines " are chiefly used as cocoa-butter substitutes in the manufacture of chocolate, from

which a portion of the true cocoa-butter has been
removed, in order to produce a cheaper, though perfectly
wholesome and nutritious material, thus enabling the
public to enjoy a sweetmeat at a price otherwise
impossible, and of which enormous quantities are now
made. The " stearines " are also used to some extent in
the manufacture of biscuits, notably " puff biscuits " ;
also for pharmaceutical purposes, and to a limited extent
in margarine (the whole oil being generally employed for
the latter purpose). The refined " oleine " is used for
a very large variety of dietetic purposes, where a fat
softer and of lower melting-point than whole coconut
oil is required, but chiefly as a baking fat for biscuits,
pastry and cakes. It figures largely in sweetmeats such
as toffee, caramels and in the icing of biscuits.

USES OF NON-FATTY PORTION.—Of the non-fatty por-
tions of the coconut, including the fibre, every portion
is brought into use, with the exception of the milk, which
is invariably wasted. The *fibre* is used for matting, etc.
The *husk* as fuel for the kiln-drying of the copra.

The residual *cake* (often called " poonack ") furnishes
a most valuable cattle food, the importance of which,
while readily appreciated on the continent, has not yet
been recognised in " conservative " England. Attention
has been drawn to the value of the cake by the Midland
and Dairy College in a complete series of experiments, in
which it is compared with other feeding stuffs (Analyst,
1911, xxxvi, p. 445).

The manufacture of *desiccated coconut* is a very
important industry carried out on scientific lines. This
product contains more oil than copra itself owing to the
fact that the rind, which contains less oil than the meat,
has been removed, and also to the lower moisture
content. The average percentage of oil is 68–72, and
any lower quantity must be attributed to partial removal

of the oil. This practice is by no means unknown and is carried out by various manipulations. When examining this product the presence of sugar, starch, etc., must be sought for as adulterants. Good desiccated coconut should be of a snow-white colour and have a fresh and pleasant taste of the nut, and contain not more than 0·1 per cent. of free fatty acids, calculated as oleic, on the oil present.

Coconut Shavings Oil.—In the preparation of desiccated coconut, the brown skin or rind next the shell is first removed. This rind is produced in sufficient quantity and has a sufficiently high fat content to make it worth while to express or extract the oil. This is often sold as coconut oil for want of a better description. Its analytical figures (see p. 86) show marked divergence from those of whole coconut oil. These differences have on occasion led to the condemnation of this product as coconut oil adulterated with other oils, and care should therefore be taken in condemning coconut oils with abnormal figures.

Analysis of Coconut Oil Cake.

Moisture	12·22
Oil	7·50
Albuminoids* . .	19·37
Digestible carbohydrates	42·33
Woody fibre . . .	12·10
Mineral matter† . . .	6·48
	100·00

* Including nitrogen, 3·10 per cent.   † Including sand, 0·92 per cent.

Coconut Oil.

Determination.	Usual limits.	Typical specimen.
Melting-point ° C., incipient fusion	$20°$ to $22°$	$22°$
,, ,, ,, complete fusion	¯$23°$ to $26°$	$26°$
Solidifying point ° C.	$22°$ to $23\frac{1}{2}°$	$23\cdot2°$
Saponification value . .	255 to 258	$257\cdot3$
Refractive index at 40° C. (Zeiss butyro-refractometer) .	$34\cdot7$ to $35\cdot5$	$35\cdot2$
Iodine value (Wijs)	$7\cdot9$ to $8\cdot8$	$8\cdot62$
Specific gravity, $\frac{15°}{15}$ C.	—	—
,, ,, $\frac{99°}{15}$ C.	$0\cdot869$ to $0\cdot874$	$0\cdot8698$
Free fatty acids (as oleic)	3 to 7 per cent.*	$0\cdot09$ per cent.†
Unsaponifiable matter . .	$0\cdot15$ to $0\cdot3$ per cent.	$0\cdot18$ per cent
Melting-point of fatty acids ° C. .	$22°$ to $26°$	$25°$
Special values :		
Reichert-Meissl . . .	6 to 8	$7\cdot5$
Polenske .	15 to 18	$16\cdot5$
Kirschner .	$1\cdot6$ to $1\cdot9$	$1\cdot8$
Avé-Lallement values :		
(a) Total baryta	—	$351\cdot8$
(b) Insol. baryta	—	$294\cdot5$
(c) Soluble baryta	—	$57\cdot3$
$b - (200 + c)$.	—	$+ 37\cdot2$
Valenta No., ° C.	12 to 15	—

* Crude unrefined.   † Refined.

Determination.	Coconut " Stearine."	Coconut " Oleine."
Melting-point (complete fusion)	From $32°$ C. down to that of whole oil.	From $15°$ C. up to that of whole oil.
Solidifying point	From $29°$ C. down to that of whole oil.	From $13°$ C. up to that of whole oil.
Saponification value	From 250 up to that of whole oil.	From 262 down to that of whole oil.
Refractive index (Zeiss butyro-refracto-meter at 40° C.)	From $34\cdot6$ up to that of whole oil.	From $35\cdot7$ down to that of whole oil.
Iodine value . .	From $2\cdot0$ up to that of whole oil.	From $14\cdot0$ down to that of whole oil.
Specific gravity $\frac{99°}{15}$ C.	From $0\cdot860$ up to that of whole oil.	—

As these are manufactured products made in a great variety of melting-points, according to the extent of pressure, only the very extreme figures are given, and practically all commercial samples yield figures well between the above limits.

Palm Kernel Oil.

Source.—Seeds of *Elæis guineensis* (the African oil palm, see Frontispiece). After the palm oil has been removed from the fleshy portion of the fruit (see "Palm Oil"), the remaining seeds are freed from their shells by hand, in a somewhat primitive manner, by women and children. The decorticated kernels are imported into this country, where they are ground and crushed in a manner similar to that employed for copra and oleaginous seeds (p. 141).

Weight of 100 kernels = 85 to 120 grm.

Content of Oil.—The kernels contain 46–53 per cent. of oil, and on pressing, about 45 per cent. of oil and 55 per cent. of cake, containing about 8–10 per cent. of fat, are usually obtained.

Description of Oil.—*Appearance.*—Like coconut oil, though perhaps somewhat darker in colour.

Consistency.—Less brittle, and more greasy than coconut oil, though of higher melting-point.

Taste and smell.—The oil has a strong, very characteristic and tenacious taste and smell.

Possible Adulterants.—Not usually adulterated.

Liability to Rancidity.—Dependent on state of refinement. The crude oil rapidly becomes rancid, while the well-refined product keeps well.

Special Tests.—It is characterised by the same peculiarities as coconut oil, but the actual values are different.

Uses of Oil.—The " stearine," whole oil, and " oleine " are all used for the same purposes and in quite a similar manner to the allied products from

coconut oil. It is quite common to find mixtures of the two oils or their products. Owing to their great similarity there is considerable difficulty in estimating and detecting these oils in the presence of one another, although the experienced worker, who has by him sufficient data of these oils and their products, is able to arrive at very close approximations to their respective quantities in many cases.

" Stearine " from palm kernel oil is produced commercially of a somewhat higher melting-point than that of coconut " stearine," and the " oleine " may have a lower melting-point than that of coconut " oleine."

There has been, in the past, an idea that the keeping properties of palm kernel products were not as good as those of coconut oil, but owing to improved modern methods of refining this distinction has passed away.

MANUFACTURED PRODUCTS FROM OIL.—" Oleines " and " stearines " quite similar to those of coconut oil are made commercially. It may be worthy of note that, while in the case of coconut oil the saponification value of the " stearine " is *lower* than that of the whole oil and decreases in proportion to the rise in the melting-point, that of palm kernel " stearine," on the other hand, increases. For instance, coconut and palm kernel oils giving saponification values of 257 and 247 respectively, will both yield " stearines " having values in the neighbourhood of 250.

USES OF THE NON-FATTY PORTION.—A feeding cake or meal is obtained after pressing or extraction, very similar to that of coconut oil, but slightly inferior to that from the latter.

PALM KERNEL OIL.

Determination.	Usual limits.	Typical specimen.
	Crude oil.	Refined oil.
Melting-point, ° C., incipient fusion .	21° to 24°	25·5°
,, ,, ,, complete fusion .	26° to 29°	28·5°
Solidifying point, ° C.	24° to 26·5°	25·2°
Saponification value	245 to 248	246·2
Refractive index at 40° C. (Zeiss butyro-		
refractometer) . . .	36 to 37·5	36·8
Iodine value (Wijs) . .	14 to 19	14·65
Specific gravity, $\frac{15°}{15}$ C.	—	—
,, ,, $\frac{99°}{15}$ C. .	0·859 to 0·871	0·8702
Free fatty acids (as oleic) .	5 to 12 per cent.	0·12 per cent.
Unsaponifiable matter .		0·22 per cent.
Melting-points of fatty acids, ° C. .	26° to 29°	28·0°
Special values:		
Reichert-Meissl value .	—	5·22
Polenske value . .	—	9·82
Kirschner value . .	—	1·07
Baryta value :		
(a) Total . . .	—	336·6
(b) Insoluble . .	—	303·7
(c) Soluble . .	—	32·9
b — (200 + c)	—	+ 70·8

Determination.	Palm kernel "stearine."	Palm kernel "oleine."
Melting - point, complete fusion	From 35° C. down to that of the whole oil.	From 23° C. up to that of the whole oil.
Solidifying point .	From 32° C. down to that of the whole oil.	From 21° C. up to that of the whole oil.
Saponification value	From 252 down to that of the whole oil.	From 244 up to that of the whole oil.
Refractive index at 40° C. (Zeiss butyro-refractometer)	From 35·5 up to that of the whole oil.	From 37·5 down to that of the whole oil.
Iodine value . .	From 33·0 up to that of the whole oil.	From 30·0 down to that of the whole oil.
Specific gravity $\frac{99°}{15}$ C.	From 0·866 up to that of the whole oil.	—

As these are manufactured products made in a great variety of

melting-points, according to the extent of pressure, only the very extreme figures are given, and practically all the commercial samples yield figures well between the above limits.

Analysis of Cake.

Moisture	11·83
Fat	6·57
Albuminoids*	16·94
Carbohydrates .	47·14
Woody fibre	13·80
Mineral matter† .	3 72
	100·00

* Including nitrogen, 2·71 per cent. † Including sand, 0·52 per cent.

Cohune Oil.

SOURCE.—*Attalea Cohune* (the Cohune Palm of Honduras, Guatemala, Brazil and Guiana).

The fruit (as shown in sketch) varies considerably in size and consists of (*a*) a hard woody shell, nearly $\frac{1}{2}$ in. thick, in texture like that of the coconut. This shell
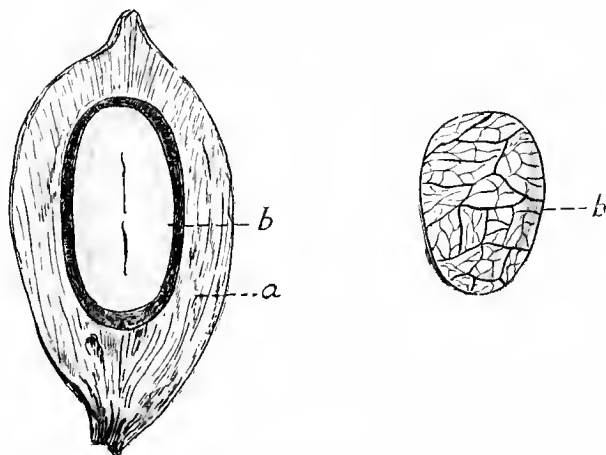
FIG. 8.—Fruit of *Attalea Cohune*: *a* = woody husk; *b* = seed.
(Natural size.)

encloses the oval seed or "kernel" (*b*), which resembles the "meat" of the coconut in taste, smell and appearance, but contains more oil, which, as will be seen from the analytical figures, is very similar in composition to coconut oil.

(The oil from *Attalea funifera* is so similar that it may be included under the head of "cohune oil," though it is sometimes distinguished under the name of "coquito" or "coquilla oil.")

Weight of 100 seeds or "kernels" = 470 grm.

The seeds or " kernels " represent 10 per cent. of the fruit.

CONTENT OF FAT (in seed).—65–72 per cent.

DESCRIPTION OF FAT.—*Appearance*.—White and solid. *Consistency*.—Rather less brittle than coconut oil.

Taste.—Pleasant nutty flavour.

Smell.—Recalling that of fresh coconuts.

SPECIAL TESTS.—High Reichert-Meissl and Polenske values, with other characteristics similar to those of coconut oil, but the slightly higher iodine value and lower solidifying point should be noted.

USES OF THE FAT.—As far as we are aware, the oil has not so far been put to any commercial use and has only been prepared on a more or less experimental scale. Several machines have been invented to remove the very solid and woody husk, but one recently devised appears to be specially suitable, and has the additional advantage of portability. As a result of this invention the immense quantity of cohune nuts available may be expected to be utilised, and large quantities of cohune oil may shortly appear on the market.

The fat will find a ready use for margarine manufacture and will doubtless be used for baking and biscuit making, for all of which purposes the refined fat will be very suitable.

Analysis of Kernels and Oil Cake.

	Kernels.		Oil cake (calculated).
Moisture	4·16	.	12·4
Oil	68·53	.	6·5
Albuminoids . .	7·12	.	21·2
Digestible carbohydrates .	13·09	.	38·8
Woody fibre . . .	5·42	.	16·1
Mineral matter . . .	1·68	.	5·0
	100·00		100·0

Cohune Oil.

Determination.	Usual limits.	Typical specimen.
Melting-point ° C , incipient fusion	—	—
,, ,, ,, complete fusion	$22°$ to $24°$	—
Solidifying point, ° C.	$19°$ to $21·5°$	$19·8°$
Saponification value	254 to 260	258·5
Refractive index at 40° C. (Zeiss butyro-refractometer)	35·2 to 36·2	35·7
Iodine value (Wijs)	9·0 to 12·5	11·92
Specific gravity, $\frac{15°}{15}$ C.	—	—
,, ,, $\frac{99°}{15}$ C.	—	—
Free fatty acids (as oleic)	Usually 0·25 to 6·0 per cent.	3·5 per cent.
Unsaponifiable matter	—	—
Melting points of fatty acids, ° C.	$25°$ to $29°$	—
Special values :		
Reichert-Meissl value	—	8·4
Polenske value .	—	15·87
Kirschner value	—	1·57
Baryta values :		
(a) Total	—	348·3
(b) Insoluble	—	292·8
(c) Soluble .	—	55·5
$b - (200 + c)$.	—	+ 37·3

Japan Tallow.

TRADE NAME.—Japan wax.

SOURCE.—The berries or fruits of *Rhus vernicifera* and *Rhus succedanea*, largely grown in Japan as the source of lacquer, the tallow being merely a bye-product. It is prepared in a very rough and ready manner, so that the product which comes on this market is often found to be mixed with the non-fatty portion of the berry and with water.

Weight of 100 berries, about 10 grm.

CONTENT OF FAT.—20 to 30 per cent.

DESCRIPTION OF FAT.—*Appearance.*—Dark green or brownish ; a bleached variety is also sold.

Consistency.—Very hard, brittle and wax-like.

Taste and smell.—Strong and characteristic. Slightly suggestive of tallow.

LIABILITY TO RANCIDITY.—Not great, after being freed from non-fatty impurities.

POSSIBLE ADULTERANTS.—Perilla oil, or other convenient vegetable oils, which are added with the intention of assisting the extraction of the tallow by rendering it more fluid, rather than for actual adulteration.

SPECIAL TESTS.—High saponification value and very high specific gravity. Iodine value low.

It should be noted that though the substance is commercially termed Japan " wax," the name is incorrectly applied, as it consists of triglycerides. Its insolubility in ether (from which it crystallises in a characteristic form of needles) and somewhat unusual solubility in hot alcohol, may afford assistance in detecting it in mixtures.

USES OF FAT.—According to Sachs (Chem. Rev.

Fett-u-Harz. Ind., 1908, xv, p. 30), 25 per cent. of Japan wax and 75 per cent. coconut "stearine" are used as a cocoa-butter substitute. It is probably not used otherwise for *edible* purposes.

JAPAN TALLOW.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	—
„ „ „ complete fusion	50° to 53°	—
Solidifying point, ° C.	47° to 50°	47·5
Saponification value	209 to 220	219·2
Refractive index at 40° C. (Zeiss butyrorefractometer) observed at higher temperature and calculated to 40° C.	47·6 to 49·7*	48·0
Iodine value (Wijs)	5 to 17	11·27
Specific gravity, $\frac{15°}{15}$ C.	0·975 to 0·999	—
„ „ $\frac{90°}{15}$ C.	0·875 to 0·877	—
Free fatty acids (as oleic)	Seldom exceeds 10 per cent.	3·12 per cent.
Unsaponifiable matter	1 to 1·5 per cent.	—
Melting-point of fatty acids, ° C.	56° to 57°	—

* Berg, Chem. Zeit., 1903, p. 755.

11

COCOA BUTTER GROUP.

1. Cocoa Butter.

2. Borneo Tallow.

3. Chinese Vegetable Tallow.

4. Palm Oil.

5. Mafura Oil and Tallow.

6. Malabar Tallow.

7. Kokum Butter.

Cocoa=Butter.

Source.—Seeds of *Theobroma Cacao*, the well-known cocoa tree, which is extensively cultivated in the tropics, and more recently in Ceylon. Cocoa-butter is a bye-product of the cocoa industry, in the manufacture of which the fat is expressed by hydraulic pressure so as to leave, as a rule, some 25 to 30 per cent. of fat in the pressed cake.

Weight of 100 seeds = 100–110 grm., but from certain districts may weigh as much as 150 grm.

Content of Fat :

    (*a*) In whole bean, 40–50 per cent.

    (*b*) In nib, 45–55 per cent.

    (*c*) In shell, 2–5 per cent.

Description of Fat.—*Appearance.*—Buttery-yellow.

Consistency.—Hard and very brittle.

Taste and smell.—Like cocoa.

Possible Adulterants.—Coconut and palm kernel " stearines," beef " stearine," " green butters," and various other hard vegetable fats.

Liability to Rancidity.—It is often stated never to go rancid. This is not strictly true, but it is certainly less susceptible to this change than almost any other fat.

Special Tests.—Björklund's test (p. 58).

As the fat is never deodourised commercially, it retains its characteristic " cocoa " smell, by which it may be recognised, even when present in reasonably small quantities with other fats.

Uses of Fat.—Chiefly in the manufacture of chocolate. For this purpose the mixture of cocoa matter

and sugar has to be incorporated with added cocoa-butter in order to allow of its being moulded, or when required for chocolate coating, to render it sufficiently fluid when warmed, for the purpose.

USES OF NON-FATTY PORTION.—Cocoa or chocolate (see Chap. VII).

COCOA-BUTTER.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	$30.5°$
,, ,, ,, complete fusion	$32°$ to $34.5°$	$33.5°$
Solidifying point, ° C.	$27°$ to $29.5°$	$29.4°$
Saponification value	192 to 198	193.5
Refractive index at 40° C. (Zeiss butyro-refractometer)	46 to 47.5	46.7
Iodine value (Wijs)	35 to 40	37.25
Specific gravity, $\frac{15}{15}°$ C.	—	0.968
,, ,, $\frac{99}{15}°$ C.	—	
Free fatty acids (as oleic)	Seldom exceeds 3 per cent.	0.65 per cent.
Unsaponifiable matter	0.8 to 1.2 per cent.	1.07 per cent.
Melting-point of fatty acids, ° C.	49 to 51	—
Special values:		
Baryta values:		
(a) Total	—	264.6
(b) Insoluble	—	261.9
(c) Soluble .	—	2.7
$b - (200 + c)$.	—	$+ 59.2$

Borneo Tallow.

Native Name.—" Minjak Tangkawang."

Source.—The seeds of various members of the family Dipterocarpeæ, of which *Shorea ghysbertiana, Shorea*
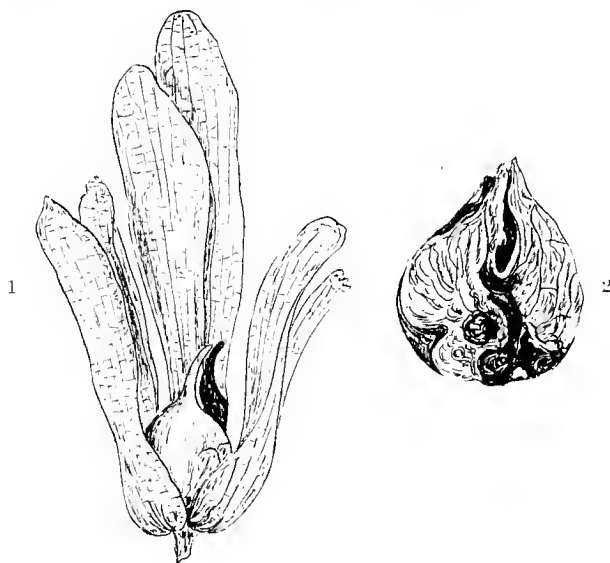
Fig. 9.—1. *Shorea robusta,* fruit. (Natural size.) 2. Portion of seed of *Shorea stenoptera,* as shipped. (Natural size.)

aptera, Shorea stenoptera, Shorea robusta, Isoptera borneensis and species of *Hopea* are among the chief representatives: they are natives of Borneo and the Straits Settlements.

The seeds are usually sent into this country under the name of " Pontianak illipé nuts," being distinguished by the prefix " large " or " small." This does not convey any botanical distinction, but is simply a

commercial differentiation of a purely dimensional character.

The nature of the fruit will be seen from the drawing of *S. robusta*; the other members of the family have, in many cases, a similar fruit varying only in size, but the persistent calyx, which forms the characteristic winged fruit, is removed before shipment. The seed itself usually splits up into two or more segments, and whole seeds are rarely seen in this country. The trees often grow in the vicinity of the sea, and the seeds, falling therein, are carried by tidal influences into various spots where they collect and are salved by the natives. Owing to the various botanical sources of these seeds, it follows naturally that samples of the fat vary somewhat in their analytical figures. The limits given by us are selected from figures obtained from a very large number of samples.

CONTENT OF FAT.—In seed, 47–60 per cent.

DESCRIPTION OF FAT.—*Appearance.*—Yellow to green solid fat, easily bleaching.

Consistency.—Hard and brittle, resembling cocoa-butter.

Taste and smell.—The taste of the native-prepared fat is most unpleasant, and the product is very crude, but that produced by modern European processes often has only a very slight taste, and a smell which is somewhat suggestive of cocoa-butter.

SPECIAL TESTS.—The analytical figures are very similar to those of cocoa-butter and afford no means of distinguishing one from the other. On applying Björklund's test this fat behaves in a very similar manner to cocoa-butter.[1]

[1] Many methods of distinguishing these fats from true cocoa-butter have been proposed, but are not satisfactory. The authors hope shortly to publish some work on this subject.

Uses of Fat.—As a cocoa-butter substitute.

Uses of Non-Fatty Portion.—The non-fatty portion is included among the various articles sold as " Illipé cake," and gives the following analytical figures :

Moisture					12·20
Fat					7·53
Albuminoids					11·32
Digestible carbohydrates					55·35
Woody fibre .					7·64
Mineral matter					5·96
					100·00

Borneo Tallow.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	34° to 36°	$34\cdot5^\circ$
,, ,, ,, complete fusion	$37\cdot5^\circ$ to 39°	$38\cdot2^\circ$
Solidifying point, ° C.	28° to 32°	$30\cdot0^\circ$
Saponification value	188 to 207*	194·3
Refractive index at 40° C. (Zeiss butyrorefractometer)	45 to 47	46·1
Iodine value (Wijs)	29 to 38	34·25
Specific gravity, $\frac{15^\circ}{15}$ C.	—	—
,, ,, $\frac{99^\circ}{15}$ C.	—	0·8597
Free fatty acids (as oleic)	Up to 25 per cent.† or even more	4·96
Unsaponifiable matter	0·7 to 2·0 per cent.	0·88 per cent
Melting-point of fatty acids, ° C.	49° to 51°	50°
Special values :		
Baryta values :		
(a) Total	—	267·3 to 282·9
(b) Insoluble	—	259·1 to 267·8
(c) Soluble	—	8·2 to 15·1
$b - (200 + c)$.	—	+ 50·9 to + 52·7

* Extreme limits.

† The European prepared fat contains much smaller quantities.

Chinese Vegetable Tallow.

NATIVE NAME of SEEDS—" Cây-sói."

SOURCE.—*Stillingia sebifera* (*Croton sebiferum* or *Sapium sebiferum*) Natural order Euphorbiaceæ; indi-
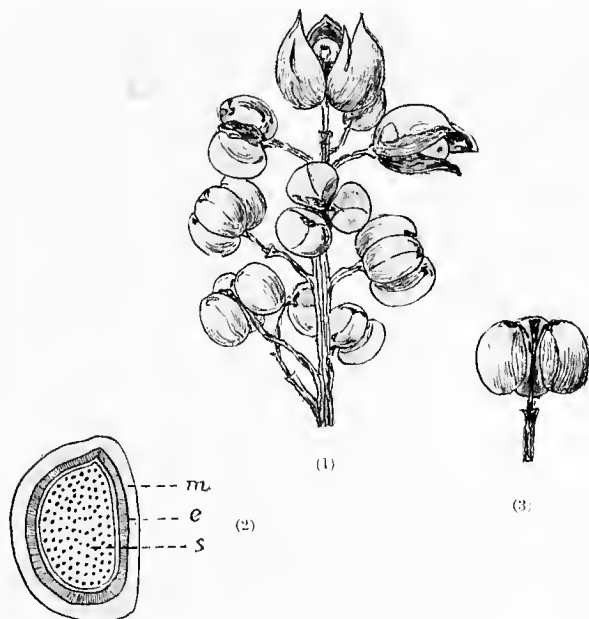
FIG. 10.—(1) Fruit of *Stillingia sebifera*, natural size. (2) Longitudinal section of single coccus × 3. *m.* Mesocarp. *e.* Endocarp. *s.* Seed. (3) Single fruit.

genous to China, but has been introduced into North India.

The fruit, Fig. 10, is a schizocarp splitting into three cocci. The brown outer husk (epicarp) falls off, leaving the tallowy layer exposed. Fig. 10 (2) shows a section of a single coccus or nutlet, which consists of :

(*m*) The white tallowy material (*mesocarp*) which envelopes the seed and contains the tallow.

(*e*) A hard brown shell (*endocarp*) enclosing—

(*s*) A small soft yellow kernel (*seed*) which contains the liquid oil.

Three commercial fatty products are obtained :—

(*a*) *Chinese vegetable tallow* (known locally as *pi-yu*) described below, obtained by steaming the seeds, in perforated vessels, which causes the tallow to run out.

(*b*) The *liquid oil*, known in this country as stillingia oil and in China as *ting-yu*, obtained by pressing the residue from the rendering of the tallow, after crushing.

(*c*) A *mixture* of the oil and tallow, produced from the whole berry in one operation, this mixture being locally known as *mou-ičou*.

Weight of 100 berries = 20 grm.

The inner kernel represents 30 per cent. of the whole berry.

Content of Fatty Matter.—20·5 per cent. of tallow; 19 per cent. of liquid oil on whole berry.

Description of Tallow.—*Appearance.*—The commercial tallow is a pale to dark green colour with a tendency to crack, while that extracted in the laboratory by means of petroleum ether from the clean berries, after separation of the kernels, is white and marble-like, a fact which rather suggests that the green colour of the commercial product is derived from leaves or stalks.

Consistency.—Very hard and brittle.

Taste and smell.—Tallow-like and characteristic.

Optical Activity (of pure tallow).—None, but the liquid stillingia oil from the kernel has a rotary power of about 10 angular degrees in a 200 mm. tube.

SPECIAL TESTS.—Saponification value slightly higher than most fats. Iodine value low (see table). It should be tested for freedom from stillingia oil, which is easily detected by its optical activity (*supra*) as well as by its high iodine value and refractive index, as shown by the following figures obtained on a sample of pure stillingia oil extracted from kernels which the authors have separated by hand.

Iodine value (Wijs) . .	187·6
Refractive index (Zeiss butyro-	
refractometer at 40° C.) . .	78·1

USES OF TALLOW.—Although very large quantities of the tallow are imported for use in the manufacture of soap and candles, small amounts are occasionally used as a means of stiffening softer edible fats. The tallow is extensively used for edible purposes in China, but the liquid stillingia oil is alleged to be poisonous—a statement which is in need of confirmation, seeing that a certain proportion of the liquid oil is most probably extracted with the tallow when crude methods are employed, but until further information is obtained on this point one must exclude from edible uses any sample which is shown by analysis to contain stillingia oil.

DESCRIPTION OF THE MIXED OIL AND TALLOW (*mou-iéou*).—This product usually consists of a hard white solid fat, but not so hard as the pure tallow and having a slightly greasy feeling which is not apparent in the latter. On keeping it rapidly develops a rancid smell and turns brown on the outside owing to the oxidation of the liquid oil.

USES OF THE NON-FATTY PORTION.—A black dye-stuff for silk is made from the leaves.

Many of the figures recorded by various observers have undoubtedly been obtained on samples which were not pure tallow, and were either admixed with small quantities of the liquid oil or were actually *mou-iéou*.

CHINESE VEGETABLE TALLOW.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion .	$50°$ to $55°$	—
„ „ „ complete fusion .	$55°$ to $65°$	—
Solidifying point .	$39°$ to $42°$	$40·3°$
Saponification value . .	199 to 206	$203·2$
Refractive index at $40°$ C. (Zeiss butyro-refractometer)	42 to 45	$44·3$
Iodine value (Wijs) .	18 to 29	$18·26$
Specific gravity, $\frac{15°}{15}$ C. .	—	—
„ „ $\frac{99°}{15}$ C. .	—	$0·8560$
Free fatty acids (as oleic) .	From 2 per cent. up-wards; sel-dom exceeds 10 per cent.	$3·42$ per cent
Unsaponifiable matter .	1 to 2 per cent.	$1·25$ per cent
Melting-points of fatty acids, ° C. . .	—	—
Optical rotation .	$0·0$	—

The two following analyses have been selected as typical of a number of samples, examined by the authors, of the commercial product *containing some of the liquid oil*.

	Containing a little liquid oil.	*Mou-iéou*.
Melting-point, ° C. . .	$43·8°$	—
Solidifying point, ° C. . .	$30·0°$	$27·7°$
Saponification value . .	$206·3$	$200·2$
Refractive index at $40°$ C. (Zeiss butyro-refractometer)	$46·1$	$47·8$
Iodine value (Wijs) . .	$32·6$	$44·2$
Specific gravity, $\frac{99°}{15}$ C. .	—	$0·8623$

Palm Oil.

SOURCE.—Fruit of *Elæis guineensis* and other species, as well as varieties of the former.

The oil palm is indigenous to West Africa; it occurs in great abundance in Sierra Leone, Senegal, Southern Nigeria, Gold Coast, French Congo, etc., never at any great distance from the sea.   It is also found in Brazil, South America, West Indies, etc., and has been introduced into Borneo, Java, and the Philippine Islands.

The fruits are borne tightly clustered together in large heads; each fruit is about one and a half inches in length by one inch in diameter, and consists of an outer fleshy portion composed of soft pulp, usually of an orange or brownish-red colour; this surrounds the palm " nut," which encloses, as a rule, one kernel, but sometimes more (Frontispiece).

The colour and size of the fruits vary somewhat in the different varieties, and of these, the varieties yielding thin-shelled nuts are more profitable, in that they yield a larger proportion of palm kernels, and a higher percentage of oil.[1]   The fruits, having been separated from the heads, are first soaked in water to soften them, after which they are roughly crushed and set aside to ferment.   The oil is separated in a very crude manner by the natives, either by skimming off that which rises to the top, or that which is liberated by boiling.

The oil liberated by boiling from the fresh fruit is called "chop oil" and is not imported, but used locally for food purposes (Lewkowitsch).

[1] Bull. Imp. Inst., 1909, p. 4.

In this way the seeds are set free and are separately treated for the production of palm kernel oil (see p. 153).

CONTENT OF OIL.—In pulp, 55–70 per cent.

DESCRIPTION OF OIL.—*Appearance*.—Granular, and possessing a characteristic shade of orange red.

Consistency.—On an average rather stiffer than tallow, but very rancid samples are much stiffer.

Taste.—Usually very rancid.

Smell.—The smell of the unrefined oil is very characteristic and not easily forgotten; to a certain extent it recalls the odour of violets.

SPECIAL TESTS.—The Liebermann-Storch test gives in the heavier liquid a blue colour tinged with green.

Halphen method.—100 c.c. of the filtered fat (filtration must be carried out at a temperature not above 70° and as quickly as possible) are immediately mixed with three times the volume of petroleum ether and shaken with 50 c.c. of 0·5 per cent. KHO. After settling out, the aqueous layer is removed and shaken with 10 c.c. of carbon tetrachloride. This is then separated, and to it, in a porcelain dish, are added 2 c.c. of a mixture of two parts carbon tetrachloride, containing 5 drops of hydrobromic acid (sp. gr. 1·19) and one part of crystallised phenol, and the whole gently mixed.

An immediate *bluish-green* colour indicates palm oil.

Owing to the presence of an enzyme in the fresh fruit which rapidly develops acidity if the fruit be allowed to stand before extraction, the oil arrives in this country in a very acid condition, the amount of free fatty acids being at least 15 per cent. but more usually nearer 50 per cent. This variation is exemplified by the following figures :

Accra addah	51·2 per cent.	Benin	37·5 per cent.
New Calabar	31·3 ,,	Red Sherbros	22·1 ,,

USES OF OIL.—The amount of refined oil is very limited, one of its uses being to colour margarines, where artificial colours are not permitted.   This limited use may be explained by the fact that the acidity cannot be profitably removed ; but there is no doubt that when, in time to come, *fresh* fruit is extracted and the present crude methods of the natives are superseded by more efficient ones, and by the use of proper machinery, a very much larger quantity of this oil will be used in margarine.   It may be noted that the neutral oil has a very low solidifying point, and would in many cases be in a melted condition during the summer in this country.

USES OF NON-FATTY PORTION.—None.

PALM OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion .	20° to 40°	—
,, ,, ,, complete fusion .	25° to 50°	49°
Solidifying point, ° C. .	35° to 40°	—
Saponification value . . .	198 to 202	199·2
Refractive index at 40° C. (Zeiss butyro-refractometer)	41 to 45	42·0
		56·3
Iodine value (Wijs) .	52 to 57	
Specific gravity $\frac{15^\circ}{15}$ C.	0·921 to 0·924	—
,, ,, $\frac{99^\circ}{15}$ C. .	—	—
Free fatty acids (as oleic) .	15 to 80 per cent.	48·2 per cent.
Unsaponifiable matter . . .	—	—
Melting-point of fatty acids, ° C. .	—	—
Titer	43° to 45°	—

Mafura (or Mafoureira) Oil and Tallow.

SOURCE.—Seeds of *Mafoureira oleifera* (*Trichilia emetica*) found on the East African Coast.

The fruit (according to Daniel and McCrae, Analyst, 1908, vol. xxxiii, p. 276) is about 1·8 cm. long and contains three loculi, in each of which there is from one to three seeds, each being about $1\frac{1}{2}$ cm. long by 1 cm. broad and covered with a reddish-brown oily pulp.

The appearance of the seed is characteristic : the shell is a bright yellowish-red, with a large black spot on one side ; it encloses a brown kernel, which readily splits into two parts. In old seeds, as a result of drying, the colour of the seed is sometimes uniformly brown. As the shell of the seed is thin and brittle the kernels are easily separated.

The *oil* is obtained from the shell while the *tallow* is the product of the kernels.

Weight of 100 seeds = 35 grm.

CONTENT OF OIL AND TALLOW :

(a) Shell, 35–40 per cent. (Mafura oil).

(b) Kernel, 60–65 per cent. (Mafura tallow).

(c) Whole seed, 55 per cent. (oil and tallow).

DESCRIPTION OF OIL AND TALLOW :

APPEARANCE.—*Oil :* Very pale yellow.

Tallow : Light brown.

CONSISTENCY.—*Oil :* Liquid at ordinary temperatures, but solidifies at a few degrees above the freezing-point.

Tallow : Firm, but plastic.

Determination	Oil		Tallow	
	Authors' figures.	Daniel and McCrae.	Authors' figures.	Daniel and McCrae.
Melting-point, °C, incipient fusion	Liquid at ordinary temperatures	Liquid at ordinary temperatures	33°	29·5°—38°
„ „ complete fusion	Ditto	Ditto	41°	29·5°—38°
Solidifying point, °C.	—	5°	—	—
Saponification value	—	202·5	201·5	201·0
Refractive index at 40° C. (Zeiss butyro-refractometer)	50·0	54·6	48·5	47·3
Iodine value	70·1	66·0	44·5	48·5
Specific gravity $\frac{15°}{15°}$ C.	—	0·913	—	0·902
Free fatty acids (as oleic)	27·5 %	8·9 %	4·3 %	14·7 %
Unsaponifiable matter	—	0·8 %	—	1·2 %
		Daniel and McCrae, Analyst, 1908, vol. xxxiii, p. 276.		

Some commercial samples examined by the authors had figures of 52 for the iodine value and 48·5 for the re-fractive index. The free fatty acids varied from 14–26 per cent. One sample solidified at 32° C., while another did not solidify at 15·5° C. These were evidently mixtures of oil and tallow.

12

OPTICAL ACTIVITY.—The *oil* is inactive.

USES OF OIL AND TALLOW.—The oil is edible, and is used locally for such purposes. Some doubt seems to attach to the tallow, which has been stated to be poisonous, and must be so regarded till proof to the contrary is forthcoming.

USES OF NON-FATTY PORTION.—The cake is unsuitable for use as a cattle-food, since it is very bitter and probably possesses emetic properties.[1]

[1] Bull. Imp. Inst., 1908, vol. iv, p. 371.

Malabar Tallow (Piney Tallow).

SOURCE.—Seeds of *Vateria indica* (Dipterocarpeæ), a tree indigenous to the East Indies, and growing on the Malabar coast, etc.

The seed (Fig. 11) is enclosed in a hard, brown husk, about $\frac{1}{4}-\frac{1}{2}$ in. in thickness.
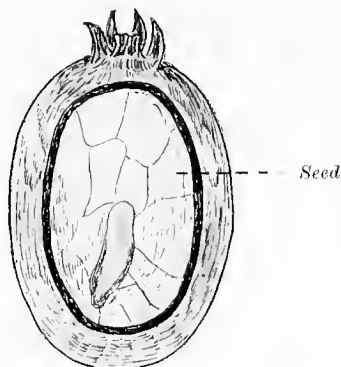
FIG. 11.—Fruit of *Vateria indica* (Malabar tallow tree). ($\frac{3}{4}$ natural size.)

CONTENT OF OIL.—49 per cent. (Lewkowitsch).

DESCRIPTION OF FAT.—*Appearance.*—Greenish-yellow to white in colour ; is easily bleached by the action of light.

Consistency.—Rather stiffer than lard.

Taste and smell.—Practically none, or very slight.

USES OF FAT.—In India it is used as an edible fat, but in other countries, as yet, only for soap and candle manufacture. The tree also yields piney resin or white dammar, used in the manufacture of varnish.

Malabar Tallow.

Determination.	Usual limits.	Authority.
Melting-point, ° C., incipient fusion .	—	
,, ,, ,, complete fusion .	$30°$ to $40°$	
Solidifying point, ° C. . .	$25°$ to $35°$	
Saponification value . . .	189 to 192	
Refractive index at $40°$ C. (Zeiss butyro-	47·5	(Crossley and Le Sueur)
refractometer)		
Iodine value .	37·8 to 39·6	(Crossley and Le Sueur)
Specific gravity $\frac{15°}{15}$ C.	—	
,, ,, $\frac{99°}{15}$ C. .	—	
Free fatty acids (as oleic) . .	5 to 15 %	(Crossley and Le Sueur)
Unsaponifiable matter .	—	—
Melting-point of fatty acids, ° C. .	$56·6°$ to $63·8°$	(Höhnel and Wolfbauer)

Kokum Butter.

SOURCE.—Seeds of *Garcinia indica*, India, East Indies, etc. The small, black ovoid seeds are enclosed in a fleshy fruit about $1\frac{1}{2}$–2 in. in diameter (Fig. 12).

The fat is, at present, only prepared by the natives by the usual crude method of boiling and clarifying.

CONTENT OF FAT.—In seed, 20–25 per cent. (Lewkowitsch).

DESCRIPTION OF FAT.—*Appearance.*—A solid, white fat.

Consistency.—Hard and brittle.

Taste and smell.—Not very pronounced.

SPECIAL TESTS.—None.

USES OF FAT.—Much employed in India as an edible fat, where it is also used as one of the many adulterants of ghee.

Recorded Constants.

Melting point*	$42 \cdot 0^{\circ}$ C.
Solidifying point .	$37 \cdot 6^{\circ}$ C. (Heise)
Saponification value*	$186 \cdot 8$
Refractive index at 40° C.* .	$46 \cdot 0$
(Zeiss butyro-refractometer)	
Iodine value* .	$34 \cdot 21$
Melting-point of fatty acids .	60°–61° C. (Heise)

* Crossley and Le Sueur, Journ. Soc. Chem. Ind., 1898, vol. xvii, p. 992.
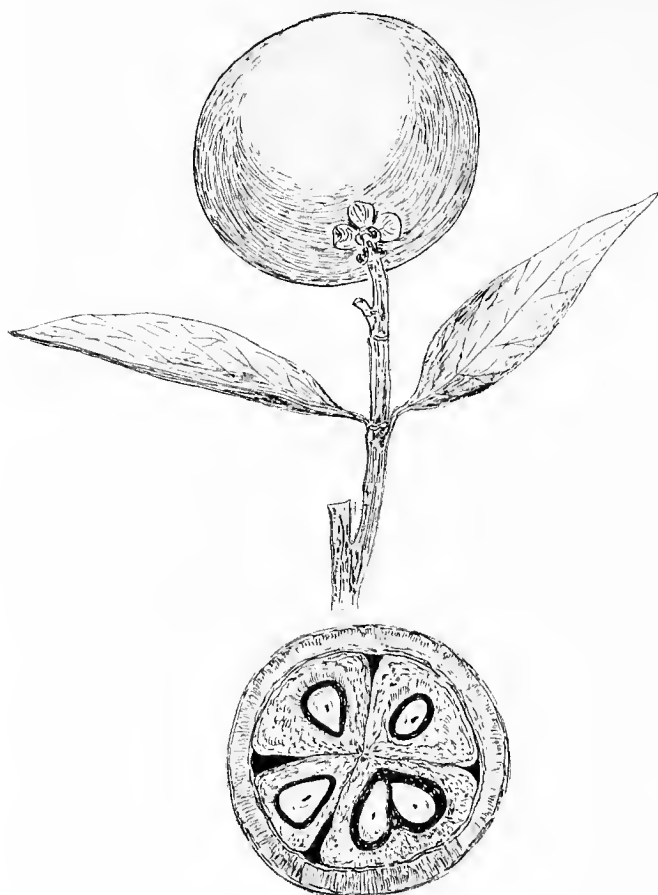
Fig. 12.—Fruits of *Garcinia indica*, Kokum fruits. (Natural size.)

THE BASSIA GROUP.

Of this group we describe :

    (1) Bassia (Butyrospermum) Parkii (Shea nut butter).

    (2) Bassia butyracea (Phulwara butter).

    (3) Mimusops Djave (Djave butter).

    (4) Bassia latifolia.

    (5) Bassia longifolia.

Of these (1) and (3) are not as a rule confused with other members of the group, but in the case of the others there has been the greatest confusion.

The two last named, owing to great similarity in appearance, are constantly shipped in a mixed condition and are also mutually confounded. For this reason we propose that the names Illipé butter, Mowrah, Mahua, Mohwrah, Phulwara fats, Mee oil, etc., be abandoned, and that the names **butyracea fat, longifolia fat** and **latifolia fat** be substituted, as by this means confusion would be avoided and identification simplified. The drawings of these seeds, here given, are to scale, and show clearly the differences of shape. The analytical figures have been obtained on the oils extracted by us from the actual seeds.

Shea Nut Oil.

TRADE NAMES.—Shea butter, Karité butter.   Other names : Bambuk butter, Galam butter.

NATIVE NAMES.—Karité, Cé, etc.

SOURCE.—*Butyrospermum* (or *Bassia*) *Parkii*. Natural Order Sapotaceæ, a large tree grown in West Africa,
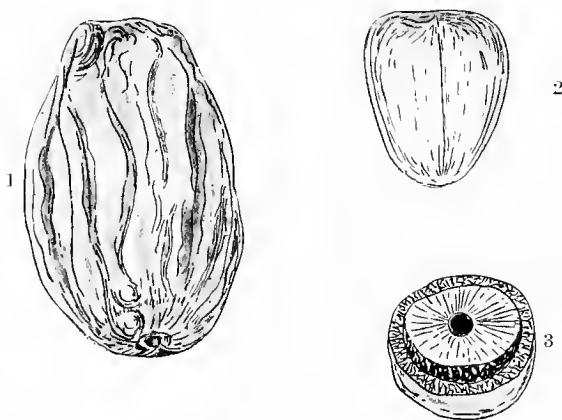
FIG. 13.—*Butyrospermum Parkii*. 1. Fruit (natural size). 2. Seed (Shea nut) ($\frac{4}{5}$ natural size). 3. Section of seed.

French Soudan, etc.   In the dried condition the fruit consists of a thin, brownish-red crinkled shell, loosely enclosing the dark-brown egg-shaped seed, which is about the size of a plum.   The kernel, which is enclosed in a glazed fragile husk, is of a chocolate colour, this colour forming a distinction between this seed and many others of a similar shape and structure, which yield a fat closely related, but at the same time distinctly different, to Shea butter.

The amount of shell varies enormously in different

specimens, according to their origin, but usually amounts to some 35–38 per cent. on the whole *seed*.

The oil is prepared in a crude manner by the natives, who remove the pulp and bury it in the earth, when fermentation takes place. In this way the seeds are liberated and are afterwards ground between stones and the fat extracted with boiling water.

Weight of 100 seeds = 344 grm.

CONTENT OF FAT.—(*a*) Whole seed, 34–44 per cent.; (*b*) kernel, 50–60 per cent.

DESCRIPTION OF FAT.—*Appearance.*—The colour of the native prepared article varies from muddy brown to a greenish grey, according to the care with which it has been prepared. The refined, bleached or European product may, however, be almost white.

> *Consistency.*—A stiff, plastic fat, somewhat granular and under certain conditions, of a "stringy" nature.
>
> *Taste and smell.*—The native-prepared article has a strong taste and smell, while the refined European product varies from little to practically no taste and smell.

SPECIAL TESTS.—Usually characterised by a high content of unsaponifiable matter, which is seldom less than 5 per cent. and often approaches 10 per cent. The crystals obtained from ether are somewhat similar in shape to those of beef fat.

Saponification value, low.

Refractive index unusually high for such a solid fat.

USES OF FAT.—The refined fat, which can be made practically tasteless and odourless, finds an increasing use for edible products, although its keeping properties are not specially good. The "oleine" is used for margarine and baking purposes, and the "stearine" finds a use as a cocoa-butter substitute.

Uses of Non-Fatty Portion.—It has been suggested that the cake should be used for cattle-feeding, but there seems to be some doubt as to its wholesomeness, and, as will be seen from the following analysis, the percentage of nitrogen is so small that its nutritive value cannot be very great.

Analysis of :

	Whole kernel.	Extracted meal.
Moisture .	5·35	. 9·76
Fat .	. 49·87 .	. 2·93
Albuminoids[1]	6·97 .	12·39
Carbohydrates	31·44	. 61·30
Woody fibre	2·99	7·46
Mineral matter .	. 3·38 .	6·16
	100·00	100·00

[1] Containing:
  Nitrogen   1·11 per cent.   1·98 per cent.

SHEA NUT OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	29° to 32°	—
,, ,, ,, complete fusion	37° to 42°	41·2°
Solidifying point, ° C.	25° to 30°	26·8°
Saponification value	180 to 190	186·9
Refractive index at 40° C. (Zeiss butyro-refractometer)	55·5 to 56·5	56·3
Iodine value (Wijs)	57 to 63	58·93
Specific gravity, $\frac{15°}{15}$ C.	—	—
,, ,, $\frac{99°}{15}$ C.	—	—
Free fatty acids (as oleic)	From 2 % upwards	8·29 %
Unsaponifiable matter	5 to 9 %	7·56 %
Melting-point of fatty acids, ° C.	—	—

Determination.	Shea nut "stearine."	Shea nut "oleine."
Melting-point, ° C., incipient fusion	40·0°	—
,, ,, ,, complete fusion	55·5°	—
Solidifying point, ° C.	34·2	24
Saponification value	179·7	181·6
Refractive index at 40° C. (Zeiss butyro-refractometer)	52·7	58·7
Iodine value	51·9	62·3
Free fatty acids	3·4 %	5·89 %
Unsaponifiable matter	6·25 %	7·72 %
Reichert-Meissl value	—	2·60
Polenske value	—	0·72

Butyracea Fat.

NATIVE NAME.—" Phulwa."

SOURCE.—The seeds of *Bassia butyracea,* which occurs in the sub-Himalayan districts, from the Ganges to Bhutan, and is found growing up to an altitude of 15,000 ft. (Bull. Imp. Inst., 1911, vol. iii, p. 229.)   The fruit consists of a thick, soft pericarp, which is blackish in colour and encloses one seed.   This seed is made up of

FIG. 14.—Seeds of *Bassia butyracea.* From Garhwal, N.W. Provinces, India.   (Natural size.)

a pale brown, highly polished, brittle shell which loosely surrounds a whitish almond-shaped kernel, smaller than that of *B. latifolia* or *B. longifolia* (compare drawings).

The seeds are known by the natives as " phulwara " and the fat as " phulwa."

Weight of 100 seeds = 78 grm. ; weight of husk = 26 per cent.

CONTENT OF FAT.—66 per cent. on kernel, 49 per cent. on whole seed.

DESCRIPTION OF FAT.—*Appearance.*—White and lard-like.

   Consistency.—Firm, and rather stiffer than lard.
   Taste and smell.—Pleasant and not very pronounced

when freshly prepared ; and if then freed from impurities its keeping properties are exceptionally good—but the crudely prepared fat rapidly develops a very strong taste and smell.

SPECIAL TESTS.—There are no special tests.   It may, however, be noted that (1) the saponification value is rather low, considering the comparatively small amount of unsaponifiable matter, and (2) there is a distinct Reichert-Meissl and Polenske value.

USES OF FAT.—Largely used as an adulterant of ghee, for which purpose it specially lends itself, any taste and smell being completely disguised by that of the ghee.

USES OF NON-FATTY PORTIONS.—None known.

For analytical values see p. 195.

Djave Butter.

NATIVE NAME OF TREE.—" Noumgou " in the Cameroons, and in Gaboon " Njave" or " Djave." The fruits are known as " Ouréré " and " Abeku " (mahogany nuts) in Gaboon and the Gold Coast Colony respectively.[1]

SOURCE.—The seeds of *Mimusops Djave* (or *Bassia*
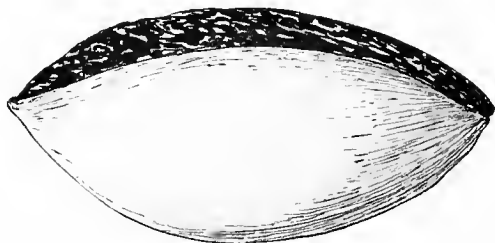
FIG. 15.—Seed of *Mimusops Djave* (Djave nut).   (Natural size.)

toxisperma), a tree belonging to the natural order Sapotaceæ and indigenous to West Africa (Gold Coast, Nigeria, etc.).

The nuts are about $2\frac{1}{2}$–3 in. long by $1\frac{1}{4}$ in. broad ; they consist of a mahogany-coloured shell, highly polished, as in the case of the other members of this group, having a long oval hilum on one side, as seen in sketch (Fig. 15).   This shell encloses a kernel which resembles a shea nut kernel in appearance, but is creamy white inside.

Weight of 100 nuts = 1850 grm. ; weight of husk = 50 per cent.

[1] Catalogue of exhibits.   Gold Coast Colony.   Franco-British Exhibition, 1908.

CONTENT OF FAT.—(a) Whole nut, about 35 per cent. ;
(b) kernel, 65–70 per cent.

DESCRIPTION OF FAT. — *Appearance.* — Like shea
butter, but much softer.

> *Consistency.*—Usually solid, but the more neutral
> samples have a very low melting-point, 60°–65° F.
> *Taste and smell.*—In no case strongly prononnced
> but vary according to mode of preparation.

USES OF FAT.—Probably at the moment only used
for soap-making, but may at any time be put to edible
use, in which case it would be necessary to render it
free from traces of hydrocyanic acid, which are derived
from the enzymic decomposition of the non-fatty
portion.

USES OF NON-FATTY PORTION.—None, owing to the
presence of a powerful cyanogenetic glucoside.

The following figures have been obtained on a sample
of the oil, extracted from the seeds with petroleum
ether by the authors :

Solidifying point °C. .	21·0
Saponification value . . .	184·2
Refractive index at 40 °C. (Zeiss butyro-refractometer) .	51·8
Iodine value (Wijs) . .	65·1
Specific gravity $\frac{99}{15}$ °C. .	0·8578
Free fatty acids (as oleic) .	9·27 per cent.
Unsaponifiable matter .	3·86 per cent.
Melting point of fatty acids °C. .	52·8
Solidifying point of fatty acids °C.	47·8

Latifolia Fat.

NATIVE NAMES.—In India *Bassia latifolia* is known under the names " mowrah," " mahua," " mahwa," etc., as well as " illupei " or " illupai," the former being Hindustani and the latter, Tamil names.[1]

SOURCE.—Seeds of *Bassia latifolia*, which occurs mainly in Central India, from Western Bengal to Burma ; it does not extend to Southern India.
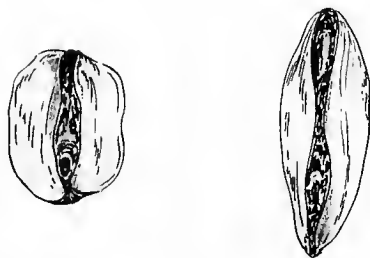
FIG. 16.—Seed of *Bassia latifolia* (natural size). From Seoni, Central Provinces, India.

The seeds are intermediate in size between those of *B. longifolia* and *B. butyracea,* the average size being shown in the sketch. As in the other members of this group, the yellowish-brown polished shell of the seed encloses a brownish-red kernel, which is usually split into two parts.

Weight of 100 seeds = 200 grm. ; weight of husk = 22 per cent.

CONTENT OF FAT.—(*a*) On whole seed, about 45 per cent. ; (*b*) on kernel, 57–60 per cent.

DESCRIPTION OF FAT.—*Appearance.*—Buttery-yellow

[1] Bull. Imp. Inst., 1911, vol. iii, p. 228.

when properly prepared, but bleaches readily on keeping. The native-made article may be very dirty and greenish in colour.

> *Consistency.*—Plastic, and rather softer and more greasy than butter.
>
> *Taste and smell.*—Pleasant when properly prepared, but the native-made article is often very disagreeable.

POSSIBLE ADULTERANTS.—The fat is often mixed with other Bassia fats, not so much as an adulteration as from the similarity of the seeds.

SPECIAL TESTS.—None.

USES OF FAT.—It is used for edible purposes in India, particularly as a substitute for tallow and as an adulterant of ghee. In Europe, its principal use at the moment is for soap and candle manufacture.

USES OF NON-FATTY PORTION.—The cake is bitter and poisonous, and is used as a manure.

For analytical values see p. 195.

Longifolia Fat.

NATIVE NAMES.—According to Sir George Watt
(The Commercial Products of India, 1908, p. 116)
Bassia longifolia is known by the same native name as
B. latifolia, but as *Bassia longifolia* only occurs in the

FIG. 17.—Seed of *Bassia longifolia.* From Madras. (Natural size.)

southern parts of India, it is usually known by its
Tamil name of " illipi " or " illupei."

SOURCE.—The seeds of *Bassia longifolia,* occurring
in Southern India *only.*

The seeds are very similar to those of *B. latifolia,*
but are longer and narrower. The fat is probably the
original " Illipé fat."

Weight of 100 seeds = 157 grm.; weight of husk =
25 per cent.

CONTENT OF OIL.—Usually about 55 per cent. on the
kernel.

DESCRIPTION OF FAT.—The fat is very similar to that of *Bassia latifolia*.

SPECIAL TESTS.—None.

USES OF FAT.—As for latifolia fat.

USES OF NON-FATTY PORTION.—The cake is poisonous, and according to the Biochemical Journal, 1910, p. 93, it contains a saponin-like glucoside. The taste is very bitter.

The following figures have been obtained by the authors for fats extracted by them from the true seeds :

Determination.	*Bassia lati-folia.*	*Bassia longi-folia.*	*Bassia buty-racea.*
Refractive index at 40° C. (Zeiss butyro-refractometer	47·7	49·3	47·8
Iodine value (Wijs)	59·4	62·6	42·6
Saponification value .	192·2	189·8	188·2
Specific gravity, $\frac{99°}{15}$ C.	0·8595	0·8624	—
Free fatty acids (as oleic)	24·6 %	3·3 %	8·74 %
Unsaponifiable matter	—	—	1·36
Baryta value :			
(a) Total	263·0	258·2	257·3
(b) Insoluble .	252·0	252·8	255·7
(c) Soluble	11·0	5·4	1·6
$b - (200 + c)$	+ 41·0	+ 47·4	+ 54·1
Reichert-Meissl value .	—	—	1·31
Polenske value	—	—	0·65

OLIVE OIL GROUP.

1. OLIVE OIL.

2. ARACHIS OIL.

3. THE ALMOND OIL GROUP.

Olive Oil.

SOURCE.—The fruits of different varieties of *Olea europœa* (one of which is shown in the sketch), the well-known olive tree, which is extensively cultivated in the countries bordering on the Mediterranean, especially Italy, Spain and France, the best oil coming from Lucca and its environs.

The oval fruit is about the size of a small plum, and varies in colour from yellowish-green to purple-green.

The oil is obtained from the fleshy portion which surrounds the seed.   Olive oil varies in quantity and quality according to the degree of ripeness of the fruit from which it is obtained, the oil from the fruit which is fully ripe being inferior, more acid, and therefore liable to develop rancidity at an earlier stage.

CONTENT OF OIL.—This is very variable, ranging from 30–65 per cent.

DESCRIPTION OF OIL.—*Appearance*.—The best quality oil is a greenish-yellow.

> *Consistency.*—A limpid oil, liquid at ordinary temperatures, and beginning to deposit " stearine " below 10° C.
>
> *Taste and smell.*—The oil is valued more particularly on its flavour.   The finest edible oil has practically no smell and very little taste, but with inferior qualities there is a distinct odour and the taste becomes sharp and unpleasant, largely due to increasing proportions of free fatty acids.   The best edible oils contain only 0·3 to 0·5 per cent. of free fatty acids, and anything much exceeding this renders it unpalatable

Fig. 18.—Fruiting branch (½ natural size) and fruits (natural size) of *Olea europæa* (olive tree).

and unsuitable for use as a salad oil. The
acidity is sometimes removed by treatment with
alkali, and oils treated in such a manner will be
characterised by very low acidity and the absence
of the absorption bands of chlorophyll which are
often clearly given by the fresh oil.

SPECIAL TESTS.—The usual constants of the oil,
though fairly characteristic, are not sufficiently re-
moved from those of many other liquid oils to enable
adulteration to be immediately detected. This will be
emphasised by the example on p. 83, and for this
reason the testing of olive oils becomes more of the
nature of special separate tests for individual adul-
terants than any sweeping search for sophistication in
general.

Halphen's, Baudouin's and Bellier's tests, followed, if
necessary, by Renard's test, should be applied. Lard
oil is sometimes used as an adulterant, and charac-
teristic crystals may usually be obtained from ether
at 0° C.

A green colour is sometimes produced by the addi-
tion of copper, which metal should therefore be tested
for in green oils.

USES OF OIL.—As a salad oil, as a packing media
for sardines, and in the country of origin for frying
purposes.

OLIVE OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	—
,, ,, ,, complete fusion	—	—
Solidifying point, ° C.	0° to 7°	2°
Saponification value	190 to 195	190·8
Refractive index at 40° C. (Zeiss butyro-refractometer)	55 to 56	55·3
Iodine value (Wijs)	80 to 87	85
Specific gravity $\frac{15°}{15}$ C.	0·915 to 0·918	0·9165
,, ,, $\frac{00°}{15}$ C.	—	—
Free fatty acids (as oleic)	0·3 to 1·0 (edible) up to 20·0 % in non-edible oil.	0·45
Unsaponifiable matter	0·5 to 2·0 %	0·8 %
Melting-point of fatty acids, ° C.	22° to 27°	—

Arachis Oil.

TRADE NAMES.—Nut oil, pea-nut oil, ground-nut oil, one of the best qualities being known as Rufisque oil (from Rufisque nuts).

SOURCE.—*Arachis hypogœa.* Natural order, *Leguminoseæ.* The origin of the plant is somewhat doubtful, but in all probability it is indigenous to America (Brazil). It is now universally cultivated in tropical and sub-tropical climates ; according to Lewkowitsch, Senegal produces the greatest quantity of fruits, and only those which are imported in the undecorticated condition are suitable for the production of the best edible oil, as the seeds alone undergo decomposition in transit, and are only fit for making " soap oils." The bulk of the seeds and fruits are imported to Marseilles.

The development of the fruit in this plant is somewhat peculiar. After flowering the young pods bend down and are forced underground to ripen ; hence the common name of " ground " or " earth nut." The fruit itself consists of a crinkled pod, or legume (erroneously called a " nut "), enclosing two or more seeds, which are covered with a membraneous brownish-red skin (Fig. 19).

Weight of 100 seeds or " kernels " = 61 grm.

CONTENT OF OIL.—In whole seed, 43–48 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Golden-yellow ; the edible oil is usually bleached to a very pale colour.

  Consistency.—Liquid at ordinary temperatures. A small deposit of " stearine " is formed at low temperatures.
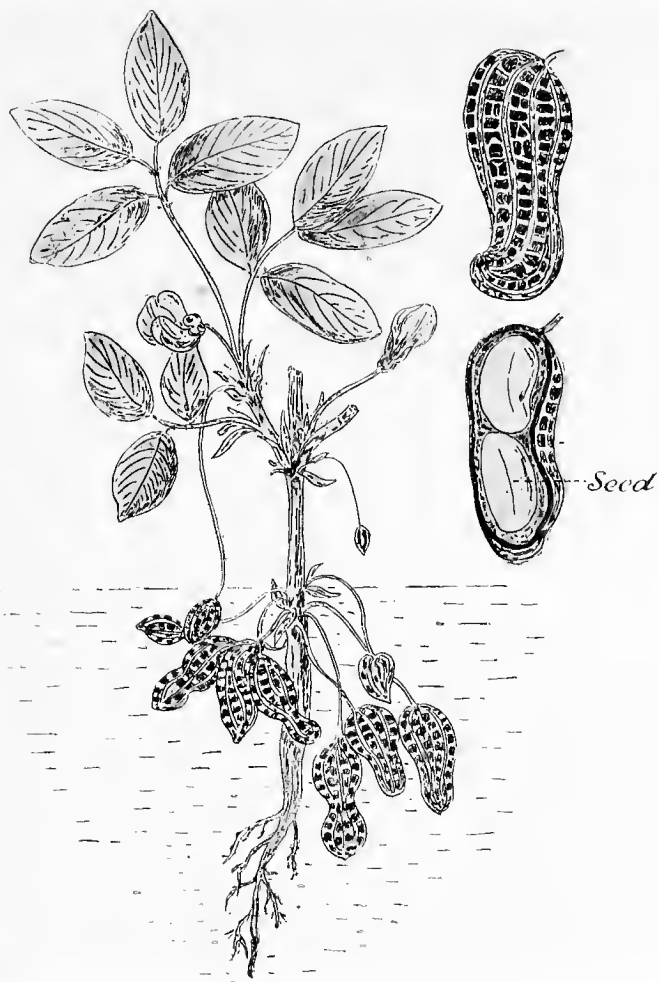
Fig. 19.—Plant (½ natural size), fruit (natural size), and seed of *Arachis hypogœa*.

Taste and *smell*.—Pleasant and nutty.

SPECIAL TESTS.—Bellier's test (p. 30) ; Renard's test (p. 34).

USUAL ADULTERANTS.—Cotton-seed, poppy, rape, maize and sesamé oils.

LIABILITY TO RANCIDITY.—Slight, and keeps well in the absence of meal, particularly that derived from the brown skin.

USES OF OIL.—Every conceivable edible purpose to which a liquid oil can be put, more particularly as a salad oil.

USES OF NON-FATTY PORTION.—The cake is very extensively used for cattle feeding, as it contains a large proportion of digestible protein.

Analysis of Ground Nut Cake (Decorticated).

Moisture . .	. 10·68
Oil . .	. 5·81
Albuminoids* . .	. 45·12
Digestible carbohydrates	30·49
Woody fibre . .	3·84
Mineral matter (ash)† .	. 4·06
	100·00

* Containing nitrogen, 7·22 per cent.   † Including sand, 0·23 per cent.

ARACHIS OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	—
„ „ „ complete fusion	—	—
Solidifying point, ° C. .	$0°$ to $5°$	—
Saponification value . . .	190 to 196	194·8
Refractive index at $40°$ C. (Zeiss butyro-refractometer)	55 to 57·5	55·5
Iodine value (Wijs) .	87 to 98	91·23
Specific gravity, $\frac{15°}{15}$ C. .	0·916 to 0·918	0·9170
„ „ $\frac{99°}{15}$ C. .	—	—
Free fatty acids (as oleic) .	Varies from 0·5 % to 20 %, rarely exceeds 10 %	5·24 %
Unsaponifiable matter . .	0·4 to 0·8 %	—
Melting-point of fatty acids, ° C.	$27°$ to $30°$	—

THE ALMOND OIL GROUP.

This group of oils includes the true almond oil, expressed from the seed of the bitter almond, *Prunus amygdalus* (var. *amara*), which is found growing in the same localities as the sweet almond, *P. amygdalus* (var. *dulcis*), viz. Morocco, the Canary Islands, Portugal, Spain, France, Sicily, Syria and Persia, and also a number of very similar oils derived from the kernels (seeds) of such fruits as peach, plum and apricot.

The fruits are drupes, and in the case of the almond it consists of :

(1) A green, velvety epicarp.

(2) A somewhat firm mesocarp.

(3) The seed or almond, covered with a cinnamon-brown testa. The epicarp and mesocarp fall off when the fruit is ripe, and have always been removed before arrival on the market. The proportion of shell to kernel varies considerably in different species.

Though the sweet variety contains more oil than the bitter, the latter is usually employed to obtain oil, as the residual cake is of more value.

The oils of this group are remarkably similar in all their properties and their detection, in the presence of one another, may be taken to be almost a practical impossibility. This is all the more unfortunate, as true almond oil is an expensive oil, whereas the others are remarkably cheap.

Of the many tests which have been described for the purpose of achieving the impossible, probably Bieber's test is the least unsatisfactory, and is recommended by Lewkowitsch, who has paid much attention to this

subject (Analyst, 1904, vol. xxix, p. 106). The test is carried out as follows :

Reagent.—Equal parts by weight of concentrated sulphuric acid, fuming nitric acid and water. It must be freshly prepared.

Five c.c. of the oil and 1 c.c. of the reagent are mixed and thoroughly shaken and the appearance of a colour change noted. The following reactions are given

Almond oil	.	.	No change.
Apricot kernel oil	.	Pink colour.
Peach kernel oil	.	A faint pink on standing.

This test serves to differentiate the oils one from another, and 50 per cent. of apricot kernel oil may be detected in almond oil, but any smaller proportion than this is uncertain. The table (p. 208), taken from the above-mentioned paper by Lewkowitsch, gives the various values which he has obtained for some of these oils, and shows very clearly the great difficulty of detecting the admixture of one with the other. The most distinctive difference is the higher iodine value given by the kernel oils in contra-distinction to almond oil, but plum kernel oil (*infra*) has practically the same iodine value as almond oil.

PLUM KERNEL OIL.

Specific gravity.	Free fatty acids.	Saponification value.	Solidifying point.	Iodine value.
At 15° C. 0·9127 to 0·9195	0·3 per cent. (*circa*)	191·5	° C. −5 to −9	100·00

Description of oil	Specific gravity.	Saponification value.	Iodine value.	Butyro-refracto-meter at 40° C.	Free fatty acids.*	Fatty acids.		Bieber's test.
						Neutralisa-tion value.	Saponifica-tion value.	
Almond oils expressed from:								
1. Valencia sweets	0·91995	207·6	99·4	57·5	2·61	207·8	207·6	Colourless.
2. Blanched valencia sweets	0·9182	191·7	103·6	57·5	1·46	196·4	201·7	,,
3. Sicily sweets	0·9178	183·3	100·3	57·0	0·39	198·8	202·2	,,
4. Mazagan bitters	0·9180	188·6	102·5	56·5	1·56	196·8	203·1	,
5. Small Indian almonds	0·91907	189·2	96·65	57·0	1·46	195·8	200·7	,,
6. Mogador bitters	0·9183	194·98	104·2	57·0	0·65	197·1	203·2	Colourless at first, then pink.
7. Peach kernel oil	0·9198	191·4	95·24	57·5	1·51	196·8	205·0	,,
8. Apricot kernel oil	0·9200	192·4	107·4	58·0	1·16	198·0	202·0	Pink colouration.
9. Apricot kernel oil from Mogador kernels	0·9172	198·2	107·9	57·0	1·41	194·0	200·7	Slightly pink.
10. Californian apricot kernel oil	0·92026	190·3	108·7	58·0	0·61	197·8	202·8	Very slightly pink.

* Calculated by authors from acid values.

RAPE OIL GROUP.

This group consists of the following oils ; all of which are derived from plants of the natural order Cruciferæ.

(1) RAPE OIL.—Obtained from the seeds of *Brassica campestris,* sub-species *napus.*

(2) RUBSEN OIL.—Distinguished in France as being the oil obtained from the seeds of *Brassica campestris,* var. *rapa.*

(3) JAMBA OIL.—The oil obtained from East Indian uncultivated seed. English rape oil is obtained from the cultivated seed.

(4) RAVISON OIL.—The variety obtained from seeds produced in the vicinity of the Black Sea.

Rape Oil.

TRADE NAME.—Colza oil.

SOURCE.—True rape oil is obtained from the seeds of
Brassica campestris (sub-species *napus*, etc.), which is
extensively cultivated in Europe and East India, large
quantities being imported from Calcutta, Ferozepore,
Guzerat, etc.   The seeds, which are very small, are
round, and vary in colour according to the sub-species
from which they are derived, some being yellow, others
brown or black.

Weight of 100 seeds = 0·37 grm.

CONTENT OF OIL.—in whole seed :

European seed.	Guzerat.	Ferozepore.
39–45 per cent.	44 per cent.	40 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Though the crude
oil is a dark brown and may contain rather a large
proportion of free fatty acids, the refined oil is a pale
yellow.

> *Consistency.*—Liquid at ordinary temperatures and
> depositing " stearine."   The oil is very viscous.
>
> *Taste.*—Unpleasant.
>
> *Smell.*—Characteristic, which is more pronounced
> in the " extracted " oil.

POSSIBLE ADULTERANTS.—Ravison, jamba, linseed,
cotton-seed, hemp-seed and particularly mineral oils.

SPECIAL TESTS.—The lowest saponification value of all
edible oils (not containing a marked quantity of un-
saponifiable matter).   *Viscosity* very pronounced, and
may be used to detect adulteration by comparing with
pure rape oil, or, according to Archbutt, with glycerine

of sp. gr. 1·226 at 15·5° C.—as castor oil alone has a higher viscosity.

The hexabromide test is characteristic in mixtures of rape oil, with liquid non-drying vegetable oils, and linseed and fish oils may be detected in rape oil by the same test.

For the lead-salt-ether method as applied to the detection of rape oil in admixture with other fats see p. 38.

Uses of Oil.—The refined oil (usually cold drawn) is sometimes used for edible purposes, but inferior qualities find an outlet as lubricants and illuminants.

Uses of Non-Fatty Portion.—Rape-seed cake is used as a cattle food.

G. Jorgensen, (Landw. Vers-Stat., 1910, lxxii, pp. 1–14; Journ. Soc. Chem. Ind., 1910, vol. xxix, p. 512, abs.) emphasises the need of a laboratory examination of this cake, as mustard-seed often becomes mixed with rape seed. The harmlessness or toxicity of the cake may be ascertained by treating the sample with white mustard and water, when if more than certain quantities of mustard oil and thiosinamine are developed in a given time the cake would be poisonous. For details, however, the original paper must be consulted.

Samples of cake yielding mustard oil have a high percentage of nitrogen and a stronger smell than normal samples. A rough test to distinguish between those likely to prove injurious to cattle and those which would be harmless, is to treat 1 grm. of the sample with water and a small quantity of white mustard and to allow the mixture to stand in a well-closed tube for one hour; in the former case the odour is much more pungent and penetrating than in the latter.

Ravison Oil.

Source. —The seeds of a wild variety of *Brassica campestris* from the Black Sea district.

Content of Oil.—In whole seed, about 35 per cent.

Description of Oil.—*Appearance.*—Amber yellow in colour, often lighter than rape oil.

    Consistency.—Liquid at ordinary temperatures, and somewhat less viscous than rape oil.

    Taste and smell.—Similar to rape oil.

Special Tests.—The oil is very similar to rape oil, for which it forms an adulterant. Its iodine value is, however, higher.

Uses of Oil.— Practically those of rape oil, but it is not so suitable for lubricating purposes.

Uses of Non-Fatty Portion.—Ravison cake is used as a cattle food.

Analysis of Ravison Cake.

Moisture .	9·04
Oil .	10·50
Albuminoids	34·37
Digestible carbohydrates	27·85
Woody fibre .	. 12·07
Mineral matter . .	. 6·17
	100·00

Jamba Oil.

Source.—The seeds of an uncultivated variety of East Indian rape.

Content of Oil.—Usually somewhat less than from cultivated rape seed.

Description of Oil.—*Appearance.*—Pale yellow.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Very strong and pronounced, as well as distinctly unpleasant.

Special Tests.—As rape oil.

Uses of Oil.—No use of the oil as an edible oil is known to the authors, but there is no reason why it should not be so used, if sufficiently refined.

The following figures give the usual limits for rape and ravison oils.

	Rape.	Ravison.
Solidifying point, ° C.	$-10°$ to -12	$-8°$ (Jean)
Saponification value	171 to 177	175 to 179
Refractive index at 40° C. (Zeiss butyro-refractometer)	59 to 60	—
Iodine value	97 to 105	109 to 122 (Archbutt)
Specific gravity at 15° C.	0·9135 to 0·9160	0·918 to 0·922 (Archbutt)
Free fatty acids (as oleic)	Up to 2 %	Up to 5 %
Unsaponifiable matter	1·4 to 3·0 % (Lewkowitsch)	1·5 to 1·75 %
Melting-point of fatty acids, ° C.	18·5° to 21·0° (Archbutt)	—
Optical activity (ang. degrees in 200 mm.)	$-0·3$ to $-0·5$	About $-0·5$

The figures for jamba oil follow those of rape oil very closely.

COTTON-SEED OIL GROUP.

1. COTTON-SEED OIL.

2. KAPOK OIL.

3. SESAMÉ OIL.

4. SOJA OIL.

5. MAIZE OIL.

Cotton-seed Oil.

TRADE NAMES.—The pure oil is usually sold in bulk under its own name, but smaller consignments under such names as " butter-oil," etc. Products consisting mainly of the oil, are sold as " Cottolene," etc.

SOURCE.—The seeds of various species of Gossypium, the cotton-plant.

The cotton fibre, with which the small black seeds are covered, having been removed by suitable machinery, without separation of the husk, the remaining seed may or may not be separated from the husk before pressing, thus forming, after pressing, the " decorticated " or " undecorticated " cake. The removal of cotton-fibre is more difficult in the case of some seeds than others. It follows, therefore, that fibre may appear in larger or smaller quantities in some undecorticated cake.

The husk constitutes about 40 per cent. of the whole seed. Weight of 100 seeds = 7 grm. (including a small amount of fibre which adheres to seed).

CONTENT OF OIL.—(a) In oleaginous portion, about 37 per cent.; (b) in whole seed, about 20 per cent.

DESCRIPTION OF OIL.—*Appearance.*—The crude oil is very dark in colour, but it is usually partially or completely refined at the mill by a simple removal of either a proportion or all of the free fatty acids by treatment with caustic soda, which at the same time removes the bulk of the colouring matter in the form of an almost purple-black dye, the resulting oil being then of a golden-yellow hue. The colour can be still further improved by bleaching. Certain tintometer standards are used in America.

Consistency.—A liquid oil which deposits on standing, particularly at low temperatures, a solid fat known as cotton-seed " stearine," for the separation of which the oil is allowed to stand in tanks, and the clear supernatant liquid having been syphoned off, the " stearine " is obtained from the deposit by filter-pressing. As more " stearine " naturally forms during the winter months, the terms " winter " and " summer " oils have become used commercially as a distinction. The " winter " oil *is more particularly used for salad purposes owing to the fact that it is less liable to produce a deposit when bottled, and as the " stearine " does not keep so well as the liquid portion, the " winter " oil is preferred for margarine and other edible purposes, though in spite of this fact the " stearine " itself is actually refined and finds a use in edible products.

Taste and smell.—Strong and distinctive ; they can seldom be so removed that they cannot be detected by the skilled palate and nose.

SPECIAL TESTS.—Halphen's reaction is characteristic (kapok oil gives a similar colour).

Note that the reaction is destroyed by heating the oil to a high temperature, though practically all the commercially refined oils give the reaction, with the exception of those treated with powerful reducing agents. (See " Hydrogenised " Oils, Appendix C.)

The fat of animals fed on cotton-seed cake may give the reaction, but always to a limited extent. In the case of heated oils, see nitric acid test (p. 101). The refractive index is on the low side for liquid vegetable oils, and the titer test is exceptionally high (33 to 36).

USES OF OIL.—The whole oil is principally used as a salad oil, and also very largely in margarines. The " stearine " is employed for lard substitutes to a limited extent. The oil also finds a large use for

cooking and frying and in cakes and biscuits. Its popularity is largely due to its cheapness, though, however well refined, it is always inclined to develop its peculiar taste and smell sooner or later.

USES OF NON-FATTY PORTION.—Apart from the well-known use of the cotton fibre, the oil cake, obtained after pressing the seed, forms one of the most popular cakes for cattle feeding.

Typical Analyses of Cotton-seed Oil Cake.

	Decorticated.		Unde-corticated.
	Chinese.	American.	
Moisture	10·52	8·65	11·32
Oil	6·29	7·93	6·16
Albuminoids*	43·50	40·25	23·75
Digestible carbohydrates	22·79	26·06	31·33
Woody fibre	10·67	10·16	21·80
Mineral matter (ash)†	6·23	6·95	5·64
	100·00	100·00	100·00
*Containing of nitrogen	6·96	6·45	3·80
† ,, ,, sand	0·12	0·23	0·42

COTTON-SEED OIL.

Determination.	Usual limits.	Typical specimen.*	Cotton "stearine."
Melting - point, ° C., incipient fusion	— —	. .	—
Melting - point, ° C., complete fusion	—	—	—
Solidifying point, ° C. .	3° to 5°	3°	19°
Saponification value . . .	192 to 195	192·6	196·2
Refractive index at 40° C. (Zeiss butyro-refractometer)	58 to 59	58·4	—
Iodine value (Wijs)†	105 to 115	112	91·2
Specific gravity $\frac{15°}{15}$ C..	0·922 to 0·925	0·9228	0·919
„ „ $\frac{99°}{15}$ C..	—	—	—
Free fatty acids (as oleic) .	Varies	0·25 %	0·08 %
Unsaponifiable matter . .	0·8 to 1·8 %	0·85 %	—
Melting-point of fatty acids, ° C.	35 to 38	—	—

* Refined edible oil. † Winter oil should not have an iodine value lower than 110 per cent.

Kapok Oil.

TRADE NAME.—Bastard cotton oil.

SOURCE.—Seeds of *Eriodendron anfractuosum* and *Bombax malabaricum*. Both trees are widely distributed in the tropics, and *E. anfractuosum* (which seems to be the chief source of kapok oil) is found in great abundance in Java, West Indies, Africa, etc.   In
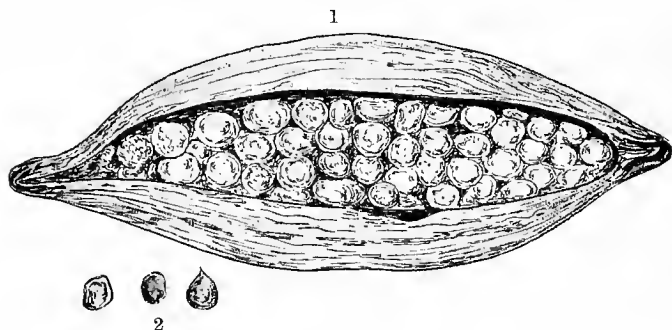
FIG. 20.—1. Half open pod of *Eriodendron anfractuosum*.   From Kordofan (¾ natural size).   2. Seeds (natural size).

some parts the tree is known as the " silk cotton tree," owing to the fact that the seeds, which are enclosed in an oval brown pod, are entirely covered with a cottony growth from the inner wall of the pod.   The seeds themselves, which are quite free from hairs (unlike cotton), are small, round, and black in colour, the hard shell constituting about 40 per cent. of the whole.[1]

The imports to Holland and America are steadily increasing.

Weight of 100 seeds = 6·0 grm.

Lewkowitsch.

CONTENT OF OIL.—On whole seed : Ceylon seed, 22 per cent. ; Calcutta seed, 24–25 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Darkish yellow.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Not unpleasant, and resembling cotton-seed oil in these respects.

SPECIAL TESTS.—Halphen's reaction positive, but the oil is distinguished from cotton oil by means of Becchi's test (modified). It is also possible to detect 1 per cent. of kapok oil in other liquid oils by this test (see p. 54).

USES OF OIL.—As cotton-seed oil, and probably large quantities are either sold as cotton-seed oil or in admixture with it. It is used as an edible oil in Holland.

Analysis of Seeds and Cake.[1]

	Seeds.	Cake.
Moisture . .	10·85	13·80
Oil	22·01	7·47
Albuminoïds	22·87	26·25
Digestible carbohydrates	18·65	23·19
Woody fibre . .	20·02	23·19
Mineral matter ·	5·60	6·10
	100·00	100·00

[1] Smetham (abs. Analyst, 1910, vol. xxxv, p. 58).

Kapok Oil.

Determination.	Usual limits.	Typical specimen.
Melting point, ° C., incipient fusion .	—	—
,, ,, ,, complete fusion .	—	—
Solidifying point .	--	—
Saponification value . .	190 to 197	192·5
Refractive index at 40° C. (Zeiss butyro-refractometer) .	53 to 57	56·2
Iodine value (Wijs) .	95 to 110	97·54
Specific gravity, $\frac{15°}{15}$ C	0·921 to 0·923	0·9217
,, ,, $\frac{99°}{15}$ C.	—	—
Free fatty acids (as oleic) .	Varies	7·54 %
Unsaponifiable matter . .	--	—
Melting-point of fatty acids, ° C. .	29° to 36°	—
Optical rotation (angular degrees in 200 mm.)	—	− 0·05

Sesamé Oil.

TRADE NAMES.—Sesamé oil, Gingelly oil.

NATIVE NAMES.—In India the white seed is known as " suffet-til " and the black as " til " or " tillie " ; other names are " beni," " benne," etc.

SOURCE.—The seeds of *Sesamum indicum* (and other varieties of the group Pedalineæ), an annual plant grown in many warm countries, such as India, China, Asia Minor, Japan, etc. In India alone (excluding Eastern Bengal and Assam) the yield was estimated at 421,900 tons, from an area of about $4\frac{3}{4}$ million acres, during 1910–11.

The fruit consists of a capsule about $1\frac{1}{2}$ in. long containing numerous small seeds. These seeds are flattened and oval with a point at one end; they are either black or white in colour, but sometimes brown or grey. The best quality oil is obtained from the white seeds, though the black variety yields a somewhat larger quantity.

Trade rules require that " white seeds " shall not contain more than 15 per cent. of black seeds and various other rules are also recognised. The Levant seeds yield the best flavoured oil.

Weight of 100 seeds = $0·28$ grm.

CONTENT OF OIL.—In whole seed, 48–54 per cent.; occasional samples, 58 per cent.

DESCRIPTION OF OIL.—*Appearance*.—Pale yellow in colour.

> *Consistency.* — Liquid at ordinary temperatures; merely a trace of " stearine " is deposited on standing.
>
> *Taste*.—Not unpleasant, rather suggestive of seaweed.

Smell.—Both taste and smell can be completely removed and the refined oil keeps well.

OPTICAL ACTIVITY.—Dextro-rotatory.

POSSIBLE ADULTERANTS.—Governed by market price. Usually rape and cotton-seed, and, more rarely, arachis oil.

SPECIAL TESTS.—The Baudouin test is distinctive, and the reaction is not given by any other commonly occurring oil. The cause of the reaction is probably not completely removable technically, but appears in the liquid fatty acids when separated. Unsaponifiable matter contains phytosterol *sesamin* and a viscid brown oil.

USES OF OIL.—The oil is used for similar purposes to cotton-seed oil, but not to such a great extent in this country as on the continent, where (in certain countries) it is required by law to form a constituent of margarine, in order to facilitate its detection in butter. It is also used as an adulterant of olive oil. The oil is very greatly used in India for various purposes, such as in cookery, as an unguent, for soaps, etc., and also as an adulterant of ghee.

USES OF NON-FATTY PORTION.—Sesamé cake is largely used for cattle feeding, more especially on the continent.

It is hard and heavy, and though in many respects it resembles linseed cake, it is lighter in colour. The nutritive value is approximately equal to that of decorticated cotton cake. In feeding trials carried out in this country sesamé cake seemed, if anything, to give slightly better results than cotton cake, though the difference is practically negligible. The proportion of fat in the milk was identical in both cases.[1] It is noteworthy that in recent experiments carried out with sesamé cake at the Agricultural College at Wye, the

[1] *Bull. Imp. Inst.*, 1909, iii, p. 309.

butter from the cows so fed, did not give the Baudouin reaction.

In some cases the whole white seeds are used as food, and in Turkey a sweetmeat called "Halvas" is made by grinding them with sugar and then cooking.

Analysis of Sesamé Cake.

Moisture .	8·19
Oil .	8·60
Albuminoids* . .	38·70
Digestible carbohydrates	25·22
Woody fibre .	5·17
Mineral matter (ash)	. 14·12
	100·00

* Containing of nitrogen, 6·2 per cent.

SESAMÉ OIL.

Determination.	Usual limits.	Typical specimen.
Melting point, ° C., incipient fusion	—	—
„ „ „ complete fusion	—	—
Solidifying point, ° C.	$-3°$ to $-4°$	—
Saponification value . .	188 to 193	191·7
Refractive index at 40° C. (Zeiss butyro- refractometer)	59 to 60·5	59·5
Iodine value (Wijs) . .	103 to 110	104·2
Specific gravity, $\frac{15°}{15}$ C.	. 0·922 to 0·924	0·9235
„ „ $\frac{50°}{15}$ C. .	—	—
Free fatty acids (as oleic) .	Varies	2·61 %
Unsaponifiable matter . .	0·8 to 1·2 %	1·02 %
Melting-point of fatty acids, ° C. . .	25° to 31°	—
Optical activity (angular degrees in 200 mm.)	$+1$ to $+3$	$+1·35$

Soja Oil.

TRADE NAMES.—Bean oil; Soya oil.

SOURCE.—The seeds of *Glycine hispida* and numerous varieties of this plant. Natural order, Leguminoseæ. Extensively cultivated in China, Japan, Manchuria and elsewhere. In the latter country the production is rapidly increasing in order to cope with the growing European demand. Practically the first shipment of the beans arrived in Hull as recently as 1908, and since then enormous quantities have been imported. During the year 1910 the total imports into this country amounted to 421,531 tons, China and Japan furnishing 174,415 and 149,958 tons respectively, Russia and other countries the remainder. In 1911, owing to increased local demand and short crops, the total imports fell to 222,657 tons. From China during the years 1910–1911 the total exports amounted to 859,407 and 650,324 tons respectively.

The whole fruit consists of a hairy pod, containing the small, round, pale yellow seeds about the size of the ordinary pea, but, if anything, rather smaller. The yellow seeds are usually employed, but green and black varieties exist, and are often found mixed with the former.

Weight of 100 seeds = 8·5 grm.

CONTENT OF OIL.—Whole seed or bean, 16–19 per cent. (commercial yield 13 per cent.)

DESCRIPTION OF OIL.—*Appearance.*—Deep brown, not much improved by alkali refining except when bleached.

Consistency.—Liquid at ordinary temperatures, and not depositing " stearine " on standing.

Fig. 21.—1. Pod of *Glycine hispida* (Soja bean). 2. Fruiting branch ($\frac{1}{2}$ natural size). 3 Seeds (natural size).

Taste and smell.—Very slight and not unpleasant. They are difficult to remove, and the keeping properties of the oil are not so good as in the case of many liquid oils, as it shows a tendency to develop a nauseous taste.

POSSIBLE ADULTERANTS.—Cotton-seed oil is the only likely adulterant on account of the cheapness of the oil.

SPECIAL TESTS.—None. Iodine value and refractive index high.

USES OF OIL.—It finds a use as an edible oil, but to a limited extent for the reason given above. It will be found in feeding cake and in biscuits made from soja meal. According to Korentschewski and Zimmermann (Chem. Zeit., 1905, xxix, pp. 777–778), practical tests showed that the oil was readily absorbed by the system and possessed a high food value.

USES OF NON-FATTY PORTION.—An excellent feeding cake extensively used on account of its high nutritive value, as it contains about 40 per cent. of protein (stated to be closely allied to casein) of very digestible nature. When first introduced in large quantities about three years ago for cattle-feeding, some sickness from over-feeding was caused before its high nutritive and digestible value was realised.

Soja flour is usually made from extracted meals, and is often adulterated with wheat, though guaranteed pure. Biscuits are made from soja meal. In its native country soja cheese and other products are made from the whole seed, both the black and white varieties being utilised in China and Japan in various ways for edible purposes.

Analyses.

	Soja bean.		Soja cake.
Moisture . . .	11·00	. .	6·01
Oil	17·03	. .	9·63
Albuminoids* . .	38·11	. .	42·00
Digestible carbohydrates	24·24	.	31·86
Woody fibre . .	4·82	. .	5·11
Mineral matter .	4·80	.	5·39
	100·00		100·00
*Nitrogen per cent. on sample 6·10		.	6·72

Soja Oil.

Determination.	Usual limits.	Typical specimen.
Melting point, ° C. incipient fusion	—	—
,, ,, ,, complete fusion	—	—
Solidifying point, ° C.	$-7°$ to $-12°$	$-11°$
Saponification value . .	190 to 193	191·8
Refractive index at 40° C. (Zeiss butyro-refractometer)	62·5 to 63·5	62·9
Iodine value (Wijs)	126 to 135	132·5
Specific gravity, $\frac{15°}{15}$ C.	0·924 to 0·926	0·9251
,, ,, $\frac{0}{15}$° C. .	—	—
Free fatty acids (as oleic) . .	Seldom exceeds 3 %	0·25 %
Unsaponifiable matter . . .	—	0·32 %
Melting-point of fatty acids, ° C. .	26 to 29	—

Maize Oil.

Trade Name.—Corn oil.

Source.—The fruits (caryopses) of *Zea Mays* (Indian corn), a large number of which are united with a fleshy stalk to form the " cob."

The fruit is commercially divided into three parts :

(1) *Bran, tp.* (testa + pericarp).

(2) *Hominy, e.* (endosperm).

(3) *Germ, s.* (scutellum).   See diagram.

Oil is obtained from the germ alone which is separated from the endosperm by various processes (washing or sifting) before pressing.   It is obtained as a bye-product in starch-making.

A very acid type of oil is obtained from alcoholic fermentation vats, but this is not now often met with and cannot be used for edible purposes.

Weight of 100 fruits = 24 grm.

Content of Oil.—(a) Whole fruit, $3-5\frac{1}{2}$ per cent. ; (b) oleaginous portion (commercially separated germ), 30–35 per cent.

Description of Oil.—*Appearance.*—Golden-yellow colour.

> *Consistency.*—Liquid, giving a small deposit of " stearine " in cold weather.

> *Taste and smell.*—A very strong tenacious taste and smell, characteristic of the original fruit ; both are removed with difficulty.

Liability to Rancidity.—Keeping qualities are fairly good when once refined, but the crude oil is rapidly hydrolised, if meal be present.

Possible Adulterants.—Only cotton-seed oil, when price permits.

SPECIAL TESTS.—Iodine value and refractive index very high. Low solidifying point, both of oil and fatty acids.

It is stated to give a small but marked Reichert-
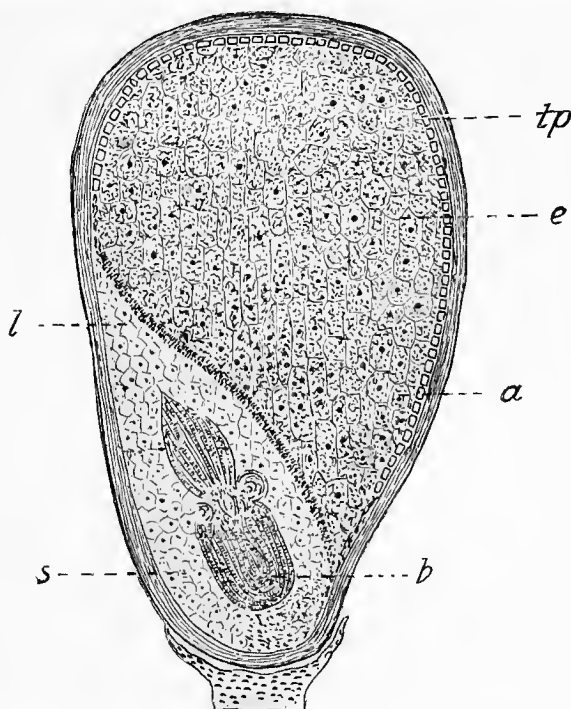
FIG. 22.—Fruit of *Zea Mays*. (Longitudinal section × 15.) *tp*. Pericarp + testa (bran). *e*. Endosperm (hominy). *s*. Scutellum (germ). *b*. Embryo. *a*. Aleurone layer. *l*. Epithelial layer.

Meissl value, but the authors' experience does not confirm this (see figures).

Unsaponifiable matter usually over 1·0 per cent. Certain varieties of the oil are characterised by a cloudiness, consisting of microscopic needle crystals, so fine as to be difficult of removal by filtration.

The melting-point of the phytosteryl acetate is higher than usual ($127°-137°$ C.).

Titer test ($16°-18°$ C.) lower than other oils of this group.

USES OF OIL.—In America the oil is extensively used for salad purposes and in margarine. Some of the better refined qualities reach a high degree of excellence as regards taste, smell and keeping properties, and therefore find a use for cake and biscuit making as well as for smearing bakers' pans. The amount of refined edible maize oil produced in this country is more limited, and the quality does not usually reach the excellence of the American product.

USES OF NON-FATTY PORTION.—The uses of the degerminated portion (hominy—*i. e.* starchy portion and bran) are too well known for comment.

A variety of products, such as flaked maize, etc., are also made.

The pressed germ forms the well-known maize cake or meal, extensively used for cattle and poultry feeding, and is a favourable vehicle for the administration of molasses, as it supplies a high protein content, together with starch and oil. The cake is most palatable.

Analysis of Maize Germ Cake.

Moisture	9·47
Oil*	12·23
Albuminoids†	20·36
Digestible carbohydrates	46·13
Woody fibre	9·38
Mineral matter‡	2·43
	———
	100·00

* Free fatty acids (per cent. on the oil), 3·8.   † Nitrogen (per cent. on the sample), 3·23.   ‡ Sand, 0·40 per cent.

Maize Oil.

Determination.	Usual limits.	Typical specimen.
Melting-point ° C., incipient fusion,	—	—
„ „ „ complete fusion	—	—
Solidifying point, ° C.	$-10°$ to $15°$*	—
Saponification value	189 to 193	191·3
Refractive index at 40° C. (Zeiss butyro-refractometer) *	59·5 to 60·5	60·3
Iodine value (Wijs)	115 to 125	119·2
Specific gravity, $\frac{15°}{15}$ C.	0·922 to 0·928	0·925
„ „ $\frac{98°}{15}$ C.	—	—
Free fatty acids (as oleic)	1 % upwards	3·34 %
Unsaponifiable matter	0·8 to 3 %	1·62 %
Melting-point of fatty acids, ° C.	18 to 20*	—
Special values :		
Reichert-Meissl	—	0·29
Polenske	—	0·38
Iodine value of liquid fatty acids †.	—	142·2 to 143·7

* De Negri and Fabris.   † Tortelli and Ruggeri.

LINSEED OIL GROUP.

1. LINSEED OIL.

2. SUNFLOWER OIL.

3. POPPY SEED OIL.

4. SAFFLOWER OIL.

5. NIGER SEED OIL.

6. CANDLE NUT OIL.

7. PARA RUBBER SEED OIL.

8. WALNUT OIL.

9. PERILLA OIL.

Linseed Oil.

SOURCE.—Seeds of *Linum usitatissimum* (the flax plant). India, America, Russia, Argentina, etc.

The variety known as Baltic Sea seed produces the purest oil, principally because the seed itself is kept free from admixture with other seeds. Black Sea seed, on the other hand, is quite commonly mixed with small quantities of such seeds as sesamé, hemp, rape, etc.

CONTENT OF OIL.—In whole seed : The figure varies somewhat according to the origin of the seed, but is usually between 36 and 40 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Golden-yellow in colour.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Strong and distinctive.

POSSIBLE ADULTERANTS.—Fish oils, cotton-seed oil, rosin oil and rape oil.

SPECIAL TESTS.—Iodine value very high (should not fall below 170 per cent.—Lewkowitsch).

Should not contain more than $2 \cdot 0$ per cent. unsaponifiable matter, or have a specific gravity below 0·931.

Hexabromide test strongly positive.

Fish oil may be detected by the smell on saponification and by the melting-point of the ether-insoluble bromides (see " Fish Oils," p. 274).

Rosin by Liebermann-Storch reaction (p. 55).

Rape oil by Tortelli and Fortini's method (p. 38), and by reduction in saponification value (in absence of mineral oils).

Traces of other oils in Black Sea oils may be due to admixture of other seeds before pressing.

USES OF OIL.—The refined oil when practically

tasteless and odourless finds a limited but somewhat increasing use as an edible oil, chiefly in margarine, but sometimes as a salad oil.

USES OF NON-FATTY PORTION.—This portion forms one of the most extensively used cattle cakes, though the seed contains a cyanogenetic glucoside, as well as an enzyme capable of decomposing it. This, however, is destroyed by the high temperature to which the meal is subjected in the course of pressing.

Analysis of Linseed Cake.

(English average. Smetham, Analyst, 1910, vol. xxxv, p. 56, abs.)

Moisture	.	.	11·16
Oil	.	.	9·50
Albuminoids	.	.	29·50
Digestible carbohydrates	.		35·54
Woody fibre	.	.	9·10
Mineral matter	.	.	5·20

100·00

LINSEED OIL.

Determination.	Usual limits.
Melting-point, ° C , incipient fusion	—
,, ,, ,, complete fusion	$-16°$ to $-20°$ (Glaessner)
Solidifying point, ° C.	$-27°$ (Chateau)
Saponification value	189 to 195
Refractive index at 40° C. (Zeiss butyro-refractometer)	73 to 75
Iodine value (Wijs)	175 to 200
Specific gravity, $\frac{15°}{15}$ C.	0·931 to 0·938
,, ,, $\frac{99°}{15}$ C.	—
Free fatty acids (as oleic)	Usually under 5 %
Unsaponifiable matter .	0·8 to 2 %
Melting-point of fatty acids .	—
Optical rotation (angular degrees in 200 mm.)	$-0·1$

Sunflower Oil.

Source.—The fruits (achenes) of *Helianthus annuus*
(Common Sunflower).   The plant is indigenous to
Mexico, but is now extensively cultivated in South
Russia, China, Hungary, South Africa, etc., in fact, in
the last-named country it is so plentiful that it is used
to mark out the boundaries of the fields.   It is an ex-
tremely easy plant to grow and the production of fruits
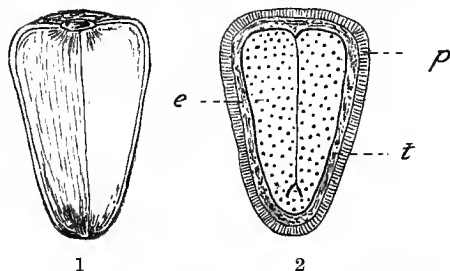
Fig. 23.—Fruits of *Helianthus annuus* (Common Sunflower.   × 3).
1. Whole fruit.   2. Longitudinal section.   *p*. Pericarp.   *t*. Testa
(or seed coat).   *e*. Endosperm.

is enormous, but attempts to introduce it into India and
the United States have not proved entirely satisfactory.
The production of Rhodesian seeds is increasing, while
quite recently Spain has been suggested as a most suit-
able country for their cultivation.   In Great Britain,
though the climate is eminently suitable for the growth
of the sunflower plant, the crop is extremely small,
chiefly due to the fact that the value of the crop is
but little known and much prejudice has to be over-
come.

The fruits (as shown in sketch) vary in colour from

white to brown or black, and are about 1 cm. in length. The smooth shell (or pericarp) which encloses the seed constitutes some 50–55 per cent. of the whole fruit, the remaining 45–50 per cent. being made up of the oleaginous seed.

Weight of 100 fruits $= 6\frac{3}{4}$ grm.

CONTENT OF OIL.— (a) whole fruit 22–25 per cent. ; (b) seed (i. e. oleaginous portion) 45–50 per cent.

The Hungarian seeds contain the most oil, often over 50 per cent.

DESCRIPTION OF OIL.—*Appearance.*—A clear pale yellow, closely resembling olive oil in many respects.

Consistency.—Liquid at low temperatures.

Taste and smell.—Pleasant, but not very pronounced.

SPECIAL TESTS.—None.

USES OF OIL.—The oil is used very largely on the continent as a salad and margarine oil, but in this country the use is limited.

USES OF NON-FATTY PORTION.—The non-fatty portion is of special value. The cake is largely used abroad as a feeding stuff owing to its high nutritive value. In the Kuban district alone nearly 40,000 tons of oilcake were produced in the year 1911, 90 per cent. of which was shipped to Denmark. Apart from the seeds, the stalks and leaves are of commercial use, the stalks being burnt to produce an ash rich in potash, which can be advantageously employed as a fertiliser. Some idea of the extent of this industry may be gathered from the fact that seven factories alone produce from £2,000,000 to £3,000,000 worth of potash annually from sunflower stalks. The stalks also contain a tough fibre.

Smetham (Analyst, 1910, vol. xxxv, p. 59, abs.) gives the following analyses of sunflower cake :

	Whole fruit.	Husked.
Moisture	7·10	7·75
Oil	7·43	10·03
Albuminoids	19·01	37·00
Digestible carbohydrates	28·93	21·14
Woody fibre	30·03	16·53
Mineral matter	7·50	7·55
	100·00	100·00

SUNFLOWER OIL.

Determination.	Usual limits.*	Typical specimen.*
Melting-point, ° C., incipient fusion	—	—
,, ,, ,, complete fusion	—	—
Solidifying point, ° C.	—	−16
Saponification value	190 to 194	191·2
Refractive index at 40° C. (Zeiss butyro-refractometer)	60 to 63	62·7
Iodine value (Wijs)	125 to 140†	133·4
Specific gravity, $\frac{15}{15}$° C.	0·924 to 0·926	0·9253
,, ,, $\frac{99}{15}$° C.		
Free fatty acids (as oleic)	1·0 to 5·0 %	1·75 %
Unsaponifiable matter	0·3 to 0·8 %	—
Melting point of fatty acids, ° C.	20° to 23°	22°
Optical rotation (angular degrees in 200 mm.)	—	0·0

* From black seeds.

† A sample of oil extracted from *white* seeds by the authors gave an iodine value of 106 and a refractive index of 58°.

Poppy Seed Oil.

SOURCE.—Seeds of *Papaver somniferum* (the Opium Poppy) and other varieties. The seeds, which vary in colour from white to brown or bluish black, are contained in the well-known poppy capsule, which is shown both whole and in section in the accompanying photograph. The plant is largely grown in France, Russia, India, Asia Minor, Persia, Egypt, etc.

The oil obtained from the different varieties of poppy seed have been divided for commercial purposes into two classes :

(1) " Huile d'œillette," obtained from grey or blue indigenous European seed.

(2) " Huile de pavot," furnished by white, brown or mottled seeds of foreign origin. " Huile d'œillette " is superior to " huile de pavot," and is of more value commercially. In a general way these two oils can be distinguished in the following manner :

On violently shaking these oils with air in a bottle, it will be noticed that (1) gives a fine emulsion of air-bubbles, so that the oil is rendered turbid, and this is not the case with (2). The froth is also more persistent than with (2). In colour also there is a slight variation : " huile d'œillette " is a bright golden-yellow as compared with " huile de pavot," which is a pale straw colour, and often requires to be coloured for general use (L. Vuaflart, Annales des Falsifications, 1909, ii, pp. 276–278).

CONTENT OF OIL.—In seed, 45–50 per cent. According to Halphen the yield of oil varies from 36–40 per cent.

16

DESCRIPTION OF OIL.—*Appearance.*—Pale straw to golden-yellow, according to source (see above).

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Vary according to source (see above).

Longitudinal section

Longitudinal section

White seed.

Blue seed

FRUITS of the OPIUM POPPY
Papaver somniferum, L.

Transverse section

Base and Apex of Fruit
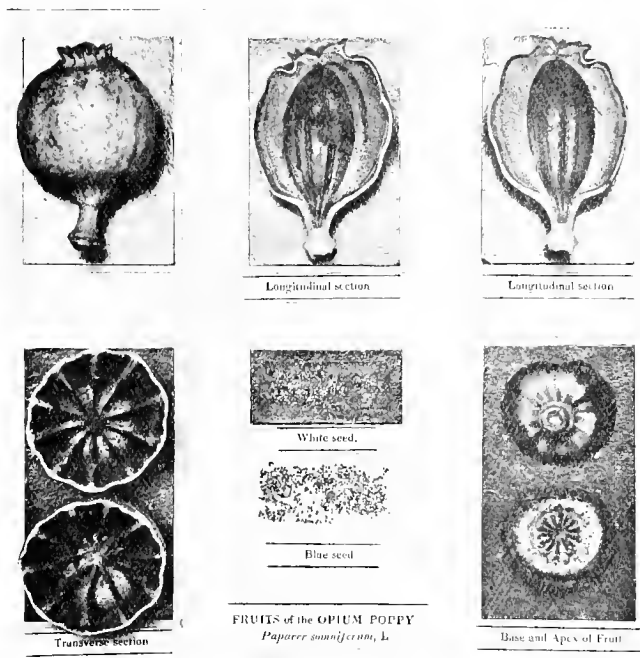
FIG. 24.

According to Halphen the cold drawn oil has a mild and pleasant odour and does not easily develop rancidity. The Russian oil, on the contrary, has a harsh disagreeable taste and its smell resembles that of linseed.

POSSIBLE ADULTERANTS.—This oil becomes mixed with sesamé oil, arachis oil, etc., not actually for the purpose of adulteration, but owing to the fact that they are often pressed in the same mill and batches of the one run through before the machinery is clear of the other. As poppy oil is usually a high priced oil, anything more than traces of other oils must be regarded as adulteration.

SPECIAL TESTS.—(See " Walnut Oil.")   Hexabromide test, no deposit.   Iodine value and refractive index very high.   Titer test low (16° C.).

USES OF OIL.—The finest oil is largely used for edible purposes, both mixed with olive oil and as a salad oil.

USES OF NON-FATTY PORTION.—The cake is used for cattle feeding and is rich in protein.

For analysis of cake see p. 244.

POPPY SEED OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	—
„ „ „ complete fusion	—	—
Solidifying point, ° C.	−15 to −18	—
Saponification value	192 to 196	194·0
Refractive index at 40° C. (Zeiss butyro refractometer)	63·0 to 64·5	63·3
Iodine value (Wijs)	130 to 138	135·6
Specific gravity, $\frac{15°}{15}$ C.	0·924 to 0·926	0·9247
„ „ $\frac{0°}{15}$ C.	—	—
Free fatty acids (as oleic)	Varies, but seldom exceeds 10 %	0·82 %
Unsaponifiable matter	About 0·5 %	—
Melting-point of fatty acids, ° C.	20° to 21°	—
Optical rotation (angular degrees in 200 mm.)	−0·02 to −0·25	—

Analysis of Poppy Seed Cake.

Moisture	. .	10·97
Oil	. .	8·63
Albuminoids*	. .	35·90
Digestible carbohydrates		20·80
Woody fibre	.	9·95
Mineral matter		13·75
		100·00

* Including nitrogen, 5·75 per cent.

Safflower Oil.

TRADE NAME.—Carthamus oil.

SOURCE.—The seeds of *Carthamus tinctorius*, one of the Compositæ. It grows in China, India, Egypt and the Levant, but it is also cultivated in many European countries for the yellow dye obtained from the flowers (this last is often confused with saffron, which is, however, quite distinct).

The seeds (known as Kurdee seeds) have a hard, shining, yellowish-white husk, the decorticated seed being said to yield a better quality oil (Tylaikow). They are 6–8 mm. long and 4–5 mm. broad (Fendler).

Weight of 100 seeds = 5 grm.

The kernels represent 54 per cent. of the whole seed (Fendler).

CONTENT OF OIL.—In seed, 25–30 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Golden yellow.

    Consistency.—Liquid at ordinary temperatures.

    Taste and smell.—Very slight.

LIABILITY TO RANCIDITY.—Decided.

SPECIAL TESTS.—Gives the hexabromide reaction, and has distinct acetyl value.

USES OF OIL.—Utilised in India for edible purposes. It serves a similar purpose as linseed oil, but its drying powers are not so great.

The following analyses of the cake are due to Smetham (Analyst, 1910, vol. xxxv, p. 54, abs.) :

	Whole seed.	Decorticated.
Moisture	8·55	11·60
Oil	9·73	7·70
Albuminoids	20·25	47·88
Digestible carbohydrates	25·12	19·72
Woody fibre	32·95	6·20
Mineral matter	3·40	6·90
	100·00	100·00

SAFFLOWER OIL.

Determination.	Usual limits.
Melting-point, ° C., incipient fusion .	—
,, ,, ,, complete fusion .	− 5° (Fendler)
Solidifying point, ° C. .	Below − 18°
Saponification value	190 to 194
Refractive index at 40° C. (Zeiss butyro-refractometer)	63 to 65
Iodine value (Wijs) .	135 to 145
Specific gravity, $\frac{15°}{15}$ C. .	0·926
,, ,, $\frac{99°}{15}$ C. .	—
Free fatty acids (as oleic) .	About 6 % (varies)
Unsaponifiable matter . .	0·7 % (Fendler)
Melting-point, ° C., of fatty acids .	16° to 17°
Special value—	
Acetyl value (true) . .	16·1 (Lewkowitsch)

Niger Seed Oil.

SOURCE.—The achenes of *Guizotia abyssinica* (Natural order Compositæ), indigenous to many districts of tropical Africa, and cultivated in other parts of the world.

The achenes are black and highly polished, about 4 mm. long and from $1\frac{1}{2}$ to 2 mm. broad.

Weight of 100 fruits = 0·35 grm.

CONTENT OF OIL.—On whole fruit, 40–50 per cent.

The shell constitutes about 20 per cent. of the achene.

DESCRIPTION OF OIL.—*Appearance.*—Yellow.

Consistency.—Liquid at ordinary temperatures.

Taste.—Pleasant and nutty.

Smell.—Very slight.

SPECIAL TESTS.—None, but is differentiated from rape oil, for which it is used as an adulterant, by its higher iodine and saponification values.

USES OF OIL.—As an edible oil, but inferior varieties find a use in soap making.

USES OF NON-FATTY PORTION.—The cake may be used for cattle feeding, and is very rich in albuminoids.

The following analysis is due to Smetham (Analyst, 1910, vol. xxxv, p. 54, abs.).

Moisture	8·90
Oil	14·03
Albuminoids	34·06
Digestible carbohydrates	21·80
Woody fibre	9·26
Mineral matter	11·95
	100 00

NIGER SEED OIL.

Determination.	Usual limits.
Melting-point, ° C., incipient fusion	—
„ „ „ complete fusion	—
Solidifying point, ° C.	$-8°$ to $-10°$
Saponification value	189 to 192
Refractive index at 40° C. (Zeiss butyro-refractometer)	63 to 64·5
Iodine value (Wijs)	128 to 134
Specific gravity, $\frac{15°}{15}$ C.	0·925 to 0·927
„ „ $\frac{99°}{15}$ C.	—
Free fatty acids (as oleic)	Varies from 2 % upwards
Unsaponifiable matter	—
Melting-point of fatty acids, ° C.	$26°$ to $28°$

Candle Nut Oil.

OTHER NAMES.—Kekune oil, Country Walnut oil, etc.

SOURCE.—Seeds of *Aleurites triloba*, a large tree of
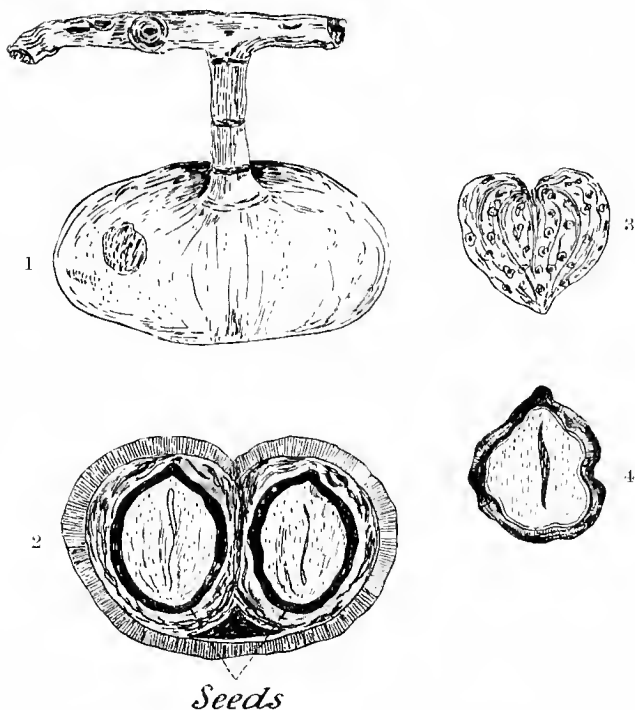
Seeds

FIG. 25.—*Aleurites triloba* (¾ natural size). 1. Fruit. 2. Section of fruit. 3. Seed (candle nut). 4. Section of seed.

tropical countries, large quantities being exported from Hong Kong, Fiji, as well as Australia and New Zealand.

The seeds are about the size and appearance of a

walnut, except that they are a mottled brown and white colour. The kernel is enclosed in a somewhat tough hard shell (see sketches). Another oil derived from *A. moluccana* is also called " candle nut oil," and the two are often sold indiscriminately.

Weight of 100 seeds = 900 grm.

CONTENT OF OIL.—In kernel, 62–66 per cent.

DESCRIPTION OF OIL.——*Appearance.*—A pale yellow, almost white, limpid oil.

Consistency.—Liquid at ordinary temperatures.
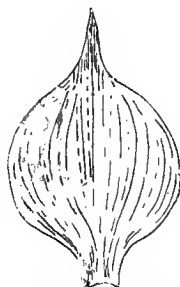
FIG. 26.—Fruit of *Aleurites Fordii* (¾ natural size).

Taste and smell.—-The cold pressed oil has not the unpleasant taste and smell of the hot pressed oil.

SPECIAL TESTS.—High iodine value. Hexabromide test positive.

USES OF OIL.——The seeds of *Aleurites triloba* are said to produce a pure edible oil, but that from *A. moluccana* (as has been pointed out by Lewkowitsch) has purging properties, so that care must be exercised in distinguishing the seeds and the products. The failure to recognise this distinction probably accounts for the wide variation in published analytical figures. There is also a sharp line of distinction to be drawn between the oil from *A. triloba,* and that from *A. Fordii* and *A. cordata,*

which are closely allied species, the fruit of *A. Fordii* being shown in Fig. 26 for the sake of comparison.

Both these species yield a poisonous oil which is employed commercially for varnishes, etc. as tung oil or Chinese wood oil.

Candle nut oil resembles linseed oil in many respects, and, seeing that it can be procured in such large quantities, is used for the same technical purposes.

USES OF NON-FATTY PORTIONS.—Smetham (Analyst, vol. xxxv, 1910, p. 55, abs.) gives an analysis of the cake as follows :

Water	7·10
Oil	16·01
Albuminoids	42·87
Digestible carbohydrates	19·92
Woody fibre.	5·95
Mineral matter	8·15
	100·00

It will be noted from the above analysis that it is exceptionally rich in albuminoids.

The authors have extracted samples of the oil from the seeds, for which they have obtained the following figures :

	Aleurites moluccana.	*Aleurites triloba* *
Saponification value	190·3	202·5
Iodine value (Wijs)	164·0	143·8
Refractive index at 40° C. (Zeiss butyro-refractometer)	65 7	61·8
Free fatty acids (as oleic) .	20·1%	1·0%

* The oil remained liquid below zero without depositing " stearine."

Rubber Seed Oil.

SOURCE.—Seeds of *Hevea brasiliensis* (the Para rubber tree). A large euphorbiaceous tree indigenous to the forests of the Amazon valley, but now very extensively cultivated in Ceylon, Borneo, Malay States, Java, etc.

The fruit, as shown in sketch, is typical of this order ; it encloses several seeds which are about the size and shape of a large damson. Each seed consists of a dark brown, smooth shell, characteristically marked with black, which shell loosely encloses the oleaginous kernel, which is covered with a cotton-like, fibrous coat.

Weight of 100 seeds = 360 grm. ; weight of kernels = 180 grm.

CONTENT OF OIL.—(*a*) In whole seed, 22–25 per cent. ; (*b*) in kernel, 45–48 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Deep brownish-yellow, about the same shade as average linseed oil.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Almost identical to those of linseed oil.

SPECIAL TESTS.—Exceptionally high iodine value and refractive index. When determining the saponification value it will be noticed that an appreciable quantity of a " gutta "-like body separates, which is insoluble in petroleum ether and is therefore not included in the unsaponifiable matter as usually estimated.

Properties.—A fairly good drying oil, producing a hard clear transparent film on exposure to the air for a period of twelve days (Pickles and Hayworth, Analyst, 1911, vol. xxxvi, p. 491). These authors also draw attention to the fact that in the liquid fatty acids (which

make up 86 per cent. of the total present), there is nearly
51 per cent. of linolic acid.
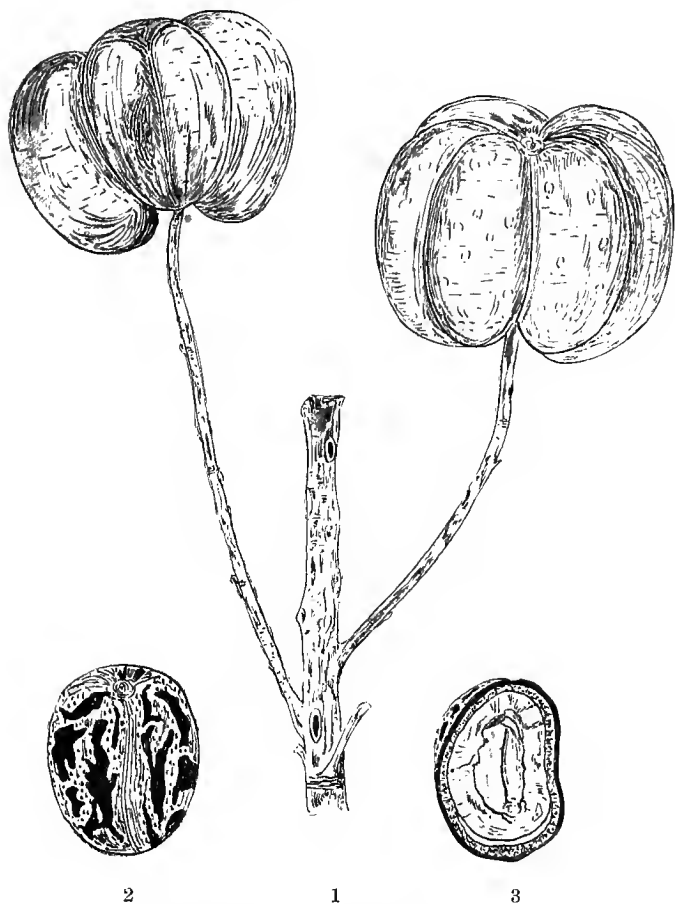
FIG. 27.—1. Fruits of *Hevea brasiliensis.* 2 Seed of ditto.
3. Section of seed. (Natural size.)

USES OF OIL.—At the present time no quantity of
the oil is prepared commercially owing to the fact that

the seeds are all required for planting purposes, but in view of the extensive area over which this tree is now being cultivated, it is inevitable that a very large quantity of the seeds will eventually be produced for which a use will have to be found, and it is therefore to be expected that in the near future the oil will appear on the market in considerable quantities, in which case it will form a substitute for linseed oil, and no doubt attempts will be made to utilise it for edible purposes, but as to its suitability in this direction we do not wish to make any definite statement—particularly since any oil intended for this purpose would have to be very carefully extracted in order to avoid as far as possible the action of the lipolytic enzyme present in the seed. According to Dunstan (Chem. Soc. Proc., 1907, vol. xxiii, pp. 168, 169) the seed kernel when ground with water evolves small quantities of hydrocyanic acid and acetone, thus indicating the presence of a cyanogenetic glucoside. There is also evidence of an enzyme capable of decomposing this glucoside.

USES OF THE NON-FATTY PORTION.—This portion is hardly likely to be utilised for edible purposes unless its poisonous properties can be counteracted, and in any case it will be necessary for extensive trials to be carried out before its value as a cattle food can be ascertained.

[1]*Analysis of Seed.*

Moisture	11·00
Oil	24·87
Albuminoids	9·63
Digestible carbohydrates	22·55
Woody fibre	30·40
Mineral matter	1·55

100·00

[1] Smetham (Analyst, 1910, vol. xxxv, p. 59, abs.).

Para Rubber-Seed Oil.

Determination.	Usual limits.	Typical specimen.
Melting-point, ° C., incipient fusion	—	—
,, ,, ,, complete fusion	—	—
Solidifying point. °C	—	—
Saponification value, ° C.	190 to 195	191·7
Refractive index at 40° C. (Zeiss butyro-refractometer)	61 to 64	62·7
Iodine value, (Wijs)	135 to 140	138·7
Specific gravity, $\frac{15°}{15}$ C.	0·924 to 0·927	0·9258
,, ,, $\frac{99°}{15}$ C.	—	—
Free fatty acids (as oleic)	Varies greatly	5·26 %
Unsaponifiable matter	—	0·53 %
Melting-point of fatty acids, ° C.	—	—
Optical rotation (angular degrees in 200 mm.)	—	− 0·04

Note.—The figures for Ceara rubber oil are not greatly different from the above.

Walnut Oil.

SOURCE.—Seeds (walnuts) of the well-known tree *Juglans regia*, indigenous to Western Asia, but now in cultivation throughout Europe, especially in Southern France.

The kernel from which the oil is obtained is too well known to require any description. The best oil is obtained by pressing kernels when they are two to three months old, as before this time a good deal of albuminous matter separates with the oil; but if, on the other hand, the kernels are kept too long, considerable hydrolysation will take place.

CONTENT OF OIL.—In kernel, 60–64 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Pale greenish-yellow to almost colourless.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Pleasant and nutty.

SPECIAL TESTS.—High iodine value and refractive index. Very low solidifying point.

Bellier's test for poppy-seed oil (Ann. chim. appliq., 1905, lii).—1 c.c. of the oil is warmed with 5 c.c. of a 16 per cent. solution of KHO in 92 per cent. alcohol till clear, the tube closed and kept at 70° for twenty minutes. To the solution is added sufficient 25 per cent. acetic acid to neutralise the KHO used (ascertained by previous trial). The tube is again corked and cooled to 25° C. and finally placed in water at 17° to 19° C., shaking frequently. Pure walnut oil only deposits a very small quantity of fatty acids after long standing, whereas poppy seed gives an abundant precipitate. It is doubtful if less than 20 per cent. of poppy-seed oil can be detected.

Halphen's test for linseed oil (Bull. Soc. Chim., 1905, xxxiii, p. 571).—0·5 c.c. of the oil are dissolved in 10 c.c. of ether and 3 c.c. of bromine solution (made by adding sufficient bromine to carbon tetra-chloride to increase the volume by one half) added. The tube is closed and the contents mixed by inversion and kept at 25° C. In the presence of linseed oil turbidity occurs in less than two minutes. Poppy seed does not interfere.

USUAL ADULTERANTS.—Principally poppy seed and linseed oils and other liquid vegetable oils.

USES OF OIL.—Owing to the demand for whole kernels the amount of oil expressed is somewhat limited, and is largely used in the manufacture of the finest artists' colours. From time to time, however, it appears as a salad oil, and sometimes as an adulterant of olive oil when the price permits.

USES OF NON-FATTY PORTION.—As a feeding stuff for cattle, but only to a limited extent.

Analyses :

	Kernel.	Cake (calculated).
Moisture	4·21	13·0
Oil	61·90	7·0
Albuminoids	18·63	44·0
Digestible carbohydrates	11·94	28·2
Woody fibre	1·26	2·9
Mineral matter	2·06	4·9
	100·00	100·0

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WALNUT OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, incipient fusion .	—	—
„ „ complete fusion . .	—	—
Solidifying point, °C.	—	−20
Saponification value	193–197	195·4
Refractive index at 40° C. (Zeiss butyro-refractometer) . .	64·5 to 67·5	64·7
Iodine value (Wijs) . .	138 to 148	140·8
Specific gravity $\frac{15°}{15}$ C. .	0·925 to 0·927	0·9256
„ „ $\frac{98°}{15}$ C. . .	—	—
Free fatty acids (as oleic) . .	Varies	3·76 %
Unsaponifiable matter . .	0·5 to 1 %	—
Melting-point of fatty acids, °C. .	15° to 20°	—

Perilla Oil.

SOURCE.—Seeds of *Perilla ocymoides* (Natural Order Labiatæ). Indigenous to N.W. Himalayas, China, and Japan. The seeds are very small, being about the size and shape of rape-seeds.

CONTENT OF OIL.—In seed, 33–35 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Dark brown.

Consistency.—Liquid at ordinary temperatures.

Taste and smell.—Like linseed oil.

SPECIAL TESTS.—The iodine value is higher than that of any known fatty oil.

USES OF OIL.—Largely used for edible purposes in the country of origin, but its use for this purpose in Europe is not known. It is, however, sometimes added to Japan wax to assist in the expression of the latter, and in this way may find its way into food products.

USES OF THE NON-FATTY PORTION.—According to Sir George Watts' Dictionary of Economic Products of India, the seeds are used as a food, and from this it may be inferred that the residual cake from the preparation of the oil may also be used as a feeding-stuff.

The following figures are due to Wijs (abs. Journ. Soc. Chem. Ind., 1903, vol. xxii, p. 805).

Specific gravity $\frac{20}{20}°$ C. . .	0·9306
Saponification value . . .	189·6
Iodine value	206·1
Free fatty acids . . .	0·48
Melting-point of fatty acids .	$- 5·0°$ C.

CASTOR OIL GROUP.

1. CASTOR OIL.
2. CHAULMUGRA OIL GROUP.

Castor Oil.

PHARMACEUTICAL NAME.—Oleum ricini.

SOURCE.—Seeds of *Ricinus communis*.

Many varieties of the plant are grown in India, which country is also the largest producer.   Large quantities of seeds are also produced in the British African Possessions, East and West Indies, North and South America, French Indo-China, Mexico, etc., and recently samples of castor seeds from Uganda, Anglo-Egyptian Soudan, Ceylon and Fiji have been examined and the
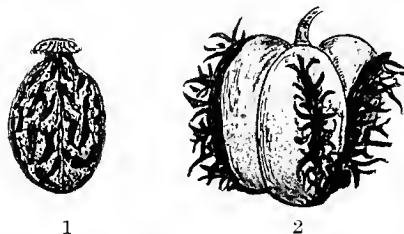
FIG. 28.—*Ricinus communis* (Castor oil tree). 1. Seed. (1½ times natural size.) 2. Fruit enclosing several seeds. (Natural size.)

oil found to be equal, and in some cases superior, to that of the Bombay seed.[1]

Seeing that there are such a large number of species cultivated, the imported seed varies very much in size, shape and markings.

The fruit is enclosed in a characteristic spiny husk, which is shown partly ruptured in the sketch.   This fruit contains several seeds, the markings on which resemble those on the Para rubber seed (see sketch, p. 253).   The soft kernel is enclosed in a thin shell,

[1] Bull. Imp. Inst., 1911, ix, pp. 17-35.

which amounts to about a fifth of the whole seed. This shell contains practically no oil.

The Indian Trade Journal, 1908, vol. ix, p. 309, and 1909, vol. xi, p. 273, mentions a process for destroying the toxic principle of castor seeds. The decorticated seeds are ground with water to a cream and poured into boiling water in order to effect the coagulation of the proteins. The solid residue, which is strained, dried, and freed from oil, gave the following composition :

Moisture	.	.	9·2	Oil	.	.	2·6
Ash	.	.	7·3	Protein		.	71·7
Fibre	.	.	5·0	Carbohydrates			4·2

Weight of 100 seeds = 48·7 grm.

CONTENT OF OIL.—(a) In whole seed, 45–50 per cent.; (b) kernel, 55–60 per cent.

DESCRIPTION OF OIL.—*Appearance.*—Very pale straw colour, varying to a greenish tint.

Consistency.—Liquid, but very viscous.

Taste.—Characteristic and unpleasant.

Smell.—Slight.

OPTICAL ACTIVITY.—Strongly dextro-rotatory.

POSSIBLE ADULTERANTS.—Cotton seed, rape and rosin oils.

SPECIAL TESTS.—Miscible in all proportions with absolute alcohol and glacial acetic acid. It should dissolve completely in three volumes of 90 per cent. alcohol at 20° C. The oil, when shaken with petroleum ether, takes up an equal volume of the solvent (in which it does not dissolve), the excess of petroleum separating out. The presence of another oil, however, causes the whole mixture to be homogeneous, so that this insoluble property of the oil cannot be used to detect adulteration. The specific gravity, acetyl value and viscosity are exceptionally high, the first being the highest of

any known fatty oil. The saponification value is low for a liquid oil. These characteristics, together with its optical activity, render its recognition a matter of no great difficulty.

Uses of the Oil.—The refined oil is never completely tasteless or odourless, as any attempt to carry the refinement too far depreciates its medicinal value very considerably. It is most extensively employed for medicinal purposes on account of its well-known aperient properties.

Uses of Non-Fatty Portion.—This portion is of no use for cattle feeding or any edible purpose owing to the presence of the poisonous alkaloid *ricin*. As previously mentioned, processes have been devised for the removal of this substance, but the idea does not seem to be greatly favoured. At present the only use of the non-fatty portion is as a manure.

The lipase from the seeds is commercially employed for " fat-splitting," and the recent experiments of Dunlap and Gilbert (Journ. Amer. Chem. Soc., 1911, vol. xxxiii, 1787) on castor oil seeds (freed from fat) seem to show conclusively that the enzyme contained in these seeds is able to synthesise fats, from an emulsion of glycerine and oleic acid.

CASTOR OIL.

Determination.	Usual limits.	Typical specimen.
Melting-point, incipient fusion	—	—
„ „ complete fusion	—	—
Solidifying point, ° C.	$-12°$ to $-18°$	$-18°$
Saponification value	175 to 185	180·2
Refractive index at 40° C. (Zeiss butyro-refractometer)	68 to 70	68·9
Iodine value (Wijs)	83 to 90	87·8
Specific gravity, $\frac{15}{15}°$ C.	0·960 to 0 967	0 963
„ „ $\frac{90}{15}°$ C.	—	—
Free fatty acids (as oleic)	Usually under 2 %	0·72 %
Unsaponifiable matter	0·3 to 0·6 %	0·35 %
Melting-point of fatty acids, ° C.	—	—
Optical rotation (angular degrees in 200 mm.)	+ 7·5 to + 9·0	+ 8·8
Special values:		
Reichert-Meissl value	1 to 2·5	—
Acetyl value (true)	146 to 150	—

CHAULMUGRA OIL GROUP.

This group of oils is distinguished by the poisonous properties of its members and also by their exceptional dextro-rotatory powers.

It consists of the following :

(1) CHAULMUGRA OIL.—Obtained from the seeds of *Taraktogenos Kurzii*.

(2) LUKRABO OIL.—Obtained from the seeds of *Hydnocarpus anthelminthica*.

(3) HYDNOCARPUS OIL.—Obtained from the seeds of *Hydnocarpus Wightiana*.

Lendrich, Koch and Schwartz, who have made an investigation of the margarines which caused the poisoning cases in Hamburg in 1910 (Zeit. Unters. Nahr. Genussm., 1911, xxii, p. 441), point out that these fats contain chaulmugric and hydnocarpic acids, and that their action is similar to that of croton oil.

Chaulmugra (or Chaulmoogra) Oil.

SOURCE.—Seeds of *Taraktogenos Kurzii*, a forest tree of Burmah, Chittagong, Assam, etc.

The fruits (according to Lendrich and others [*supra*]) are about the size of an orange, the seeds being embedded in the pulp. The dried fruit and seed have a strong, unpleasant odour.

CONTENT OF OIL.—In seed, about 40 per cent.

DESCRIPTION OF OIL.—*Appearance.*—White to whitish-yellow.

> *Consistency.* — Similar to butter but somewhat softer.
>
> *Taste.*—The fat is poisonous and a vesicant.
>
> *Smell.*—Pronounced.

OPTICAL ACTIVITY.—Strongly dextro-rotatory.

SPECIAL TESTS.—The saponification value is high but the optical activity is distinctive.

USES OF OIL.—The oil is used medicinally, and is simply referred to here on account of the fact that it has found its way into edible fats.

For values, see p. 269.

Lukrabo Oil.

NATIVE NAME OF SEEDS.—Ta-fung-tsze.

TRADE NAMES.—Marotty or Maratti oil.

SOURCE.—Seeds of *Hydnocarpus anthelminthica*, indigenous to Siam and Northern Cochin-China, whence they are exported to China.

CONTENT OF OIL.—In whole seed, 17·6 per cent.[1] (The kernels form 31 per cent. of the whole seed.)

For values, see p. 269.

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[1] Power and Barrowcliff, Journ. Chem. Soc., 1905, p. 893.

Hydnocarpus Oil.

Source.—Seeds of *Hydnocarpus Wightiana,* indigenous to the Western peninsula of India from South
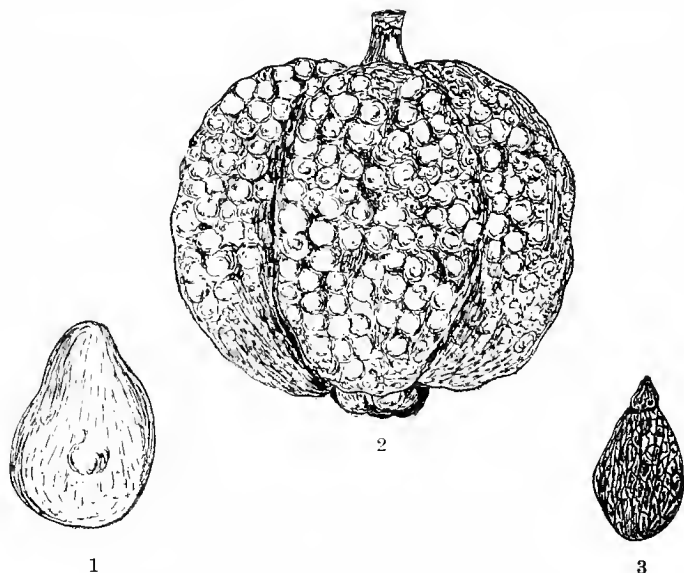
IG. 29.—1. Seed of *Taraktogenos Kurzii* (Chaulmugra). (Natural size.) 2. Fruit of *Hydnocarpus Wightiana.* ($\frac{2}{3}$ natural size.) 3. Seed of *Hydnocarpus venenata.* (Natural size.)

Concan to Travancore. (The kernels represent 75 per cent. of the whole seed.)

Content of Oil.—In whole seed, 41·2 per cent.[1]

Lukrabo and Hydnocarpus oil are somewhat similar to Chaulmugra oil, and are used for the same purposes.

[1] Power and Barrowcliff, Journ. Chem. Soc., 1905, p. 886.

Determination.	Chaulmugra oil (expressed).	Lukrabo oil.	Hydnocarpus oil (expressed).
Melting point, ° C.	$22°$ to $23°$	$24°$	$22°$ to $23°$
Free fatty acids	23·9%	11·25%	3·8%
Saponification value.	213·0	211 5	207·0
Iodine value	103·2	81·6	101·3
$[\alpha]_D^{15}$	+ 52·0	+ 44·1	+ 57·7
Authority .	Power and Gornall	Bolton and Revis	Power and Barrowcliff

For a very careful investigation into the oils of this group, see Power and Gornall (Chem. Soc. Journ., 1904, vol. lxxxv, p. 838), and Power and Barrowcliff (*ibid.*, 1905, vol. lxxxvii, p. 884).

MYRISTICACEÆ GROUP.

Of this group some values are given for the fats derived from the seeds of the following :

(1) *Myristica fragrans* (nutmeg).—Occurring in the Moluccas, East and West Indies, Banda Islands, Brazil, etc.

(2) *Myristica surinamensis* (Cuajo nut).

(3) *Myristica guatemalensis*.

(4) *Scyphocephalium Ochocoa* (Ochoco nut).

When cut in transverse section the seeds of this group
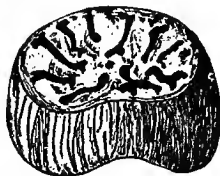
Fig. 30.—*Scyphocephalium Ochocoa ;* transverse section of seed.
(Natural size.)

show a characteristic structure, that is, the peculiar ramifications of the inner seed coat into the endosperm in the form of irregular brown strips, giving an appearance somewhat resembling marble. In longitudinal section these ingrowths are seen to arise from the chalazal end of the seed. This is typically shown in the Ochoco seed (Fig. 30), and it is this type of structure which leads to the fat being always a dark brown to black in colour, the endosperm itself, and consequently the oil, being quite white.

The fat derived from these seeds is characterised by a high percentage of the glyceride of myristic acid. They yield hard fats of tenacious character and

generally of a yellowish-brown colour, with the exception of ochoco fat, which is brown to black (*supra*).

The fats possess somewhat high melting-points and sharp and definite solidifying points. They often contain a considerable percentage of an essential oil, which, being unsaponifiable, has led to the publication of very varying figures for this value. The true saponification values are probably high and due to the presence of much myristin, which also accounts for appreciable Reichert-Meissl and Polenske values. With the exception of nutmeg butter, iodine values are low and refractive indices high. Practically pure myristin can usually be isolated from the fats by crystallisation from ether, and can be identified by preparing the myristic acid and determining the molecular weight, melting-point, etc. (molecular weight $= 228$ and melting-point $53°–54°$ C.).

The following figures will be a guide to the recognition of the fats of this group:

	Myristica fragrans (nutmeg).	Myristica surinamensis.	Myristica guatemalensis.	Scyphocephalium Ochocoa.
Fat, % in kernel .	—	70·0	59·0	59·2 (B and R)
" " seed .	38·40	59·0	50·0	—
Melting-point, ° C. .	38–51	45·0	41·0	45–48
Solidifying point, ° C. .	—	42·2	38·0	—
Saponification value .	150–180	—	223–229	238·5
Refractive index at 40° C. (Zeiss butyro-refractometer)	60–67	44·7	51·0	—
Iodine value . .	45–65	9·26	11·5–18·3	1·72
Specific gravity $\frac{98}{15}$ ° C. .	0·898	—	0·8862	—
Free fatty acids (oleic) .	9·15 %	4·6 %	14·0–19·0 %	—
Reichert-Meissl value .	—	—	1·1	0·65
Polenske value . .	—	—	5·9	4·0
Authority .	Various.	Bolton and Revis. Bolton and Revis.		Lewkowitsch.

FISH AND MARINE ANIMAL OILS.

This group of oils does not strictly come within the category of edible oils, but brief mention is made of them, since, as we have already said, it is by no means unlikely that some of them may, in the near future, be pressed into the service of the margarine manufacturer, when the present processes of de-odourisation shall have been sufficiently perfected. Even at the present time tasteless and odourless fish oils have been prepared.

The following are the main characteristics of the group :

(1) The oils are usually *liquid* at ordinary temperatures, but generally deposit " stearine " when cooled.

(2) Their *iodine values* are usually high, varying from 100 to 160 per cent. or more, being due to the presence in their glycerides of fatty acids of greater unsaturation than oleic. In fact, the degree of unsaturation surpasses that of the vegetable drying oils, in that many of the fish oils form octobromides, whereas the vegetable oils rarely form higher compounds than the hexabromides. For this reason the hexabromide test (p. 42) becomes of great value in the detection of the oils of this group.

(3) The other values which are obtained for these oils closely follow those of many vegetable oils, and do not allow of their detection in admixture with them. As just mentioned, the hexabromide test will detect these oils in other oils which do not give any reaction with that test. The reaction given by the vegetable drying oils alone would not be mistaken after a little experience for that given by the oils of this group as the precipitates are easily distinguished, but the test

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naturally does not admit of the detection of oils of this group in admixture with the vegetable drying oils (more particularly with linseed oil); for which reason they form a favourite adulterant of these oils.

The presence of fish and marine animal oils, however, may be detected by the following methods :

(a) A simple qualitative test may be carried out by saponifying the oil, when even the most highly refined fish or marine animal oil develops a characteristic fishy odour, though this may have been quite undetectable in the sample before saponification.

(b) It has been pointed out by Lewkowitsch that a real distinction can be obtained by determining the melting-point of the ether-insoluble bromides prepared from the fatty acids derived from the oil. The method of carrying out the test as slightly modified by the authors is as follows :

0·3 grm. of the fatty acids are dissolved in 5 c.c. of glacial acetic acid and 20 c.c. of methylated ether, and the solution cooled in a closed flask to 5° C. Bromine is then added, drop by drop, until its colour is permanent, the solution being kept at 5° C. during the process. If the colour on standing becomes pale yellow, a few more drops of bromine must be added. The flask is now allowed to stand at this temperature for three hours, shaking occasionally, after which the precipitate is filtered off through a folded filter and washed six times in succession with 5 c.c. of ether at 5° C., the residue after the last washing, while still moist, being placed on a piece of porous tile. The ether-insoluble bromides obtained in this manner from linseed oil melt at 180°– 183° C. (uncorrected), whereas the similar compounds derived from the fish oils have no proper melting-point, but blacken at 200° C. without melting. If, therefore, the ether-insoluble bromides derived from a linseed oil

melt at a temperature distinctly above 183° C. and show signs of blackening, the presence of fish oils may be regarded as certain. The bromides from linseed oil always melt to a *clear liquid*, and the darkening of this liquid due to the presence of even as small a quantity as 10 per cent. of fish oil can be readily seen.

(*c*) The oils prepared from the jaws of certain marine animals, particularly dolphin and porpoise, yield extremely high Reichert-Meissl values, largely due to the presence of valeric acid.

Oil.	Saponification value.	Specific gravity at $\frac{15}{15}$° C.	Iodine value.	Unsaponifiable matter.	Authority.
Whale	188·8	0·9193	110·1	1·22	Thomson and Ballantyne.
Menhaden	189·3	0·9311	160·0	1·60	Do.
Japanese fish (sardine) oil	191·4	0·9272	138·3	1·81	Bull.
Herring .	179–193·7	0·9202–0·9391	131–142	1·3–10·7	
Porpoise :					
Body	195·0	0·9258	119·4	3·7	
Jaw	269·3	0·9258	21·5	16·4	,,

RARER OILS.

1. Tiger Nut Oil.

2. Rice Oil.

3. Wheat Oil.

4. Hemp Oil.

Tiger Nut Oil.

SOURCE.—The rhizome (or tuber) of *Cyperus esculentus,* a plant common in Southern Europe. The dried tuber has a pale brown skin, which is wrinkled circumferentially in a series of rings, and the whole has a somewhat one-sided arrangement. The tissue has the texture and colour of an ordinary almond and contains much starch (see below).

These tubers are known on the Gold Coast as "Tiger nuts," and elsewhere under the name of " Chufas " and " Zulu nuts. "

Weight of 100 " nuts " (tubers) = 6 grm.

The tubers have been examined by the authors, with the following results :

Moisture	14·15
Oil	25·82
Albuminoids	5·21
Starch	22·72
Digestible carbohydrates (not starch)	24·79
Woody fibre	5·83
Mineral matter	1·48
	100·00

The " extracted " oil was of a pale yellow colour, with a pleasant taste and smell, liquid at ordinary temperatures, and gave the following figures :

Saponification value	193·2
Iodine value	74·3
Refractive index at 40° C. (Zeiss butyro-refractometer)	52·4
Free fatty acids	9·87%

It is said that in Madrid the tubers are sold for the purpose of making an iced drink.

Rice Oil.

Obtained by pressing or " extracting " rice bran.

It is of no value as an edible oil, on account of its great tendency to become rancid, but finds a use in soap manufacture.

The following figures are given by Smetham (Journ. Soc. Chem. Ind., 1893, vol. xii, p. 848).

Specific gravity $\frac{99}{99}°$ C.	.	0·8907
Saponification value		193·2
Iodine value		96·4

The use of the non-fatty portion is well known, but it has been recently shown that the consumption of the decorticated seed leads to beri-beri, which is not the case if the whole seed be ground. The husk appears to contain an anti-body to the disease (beri-beri vitamine—Casimir Funk).

Wheat Oil.

Obtained from the germ of the wheat seed. It is of little commercial value, particularly as it is very liable to become rancid.

Frankforter and Harding give the following figures :

Specific gravity $\frac{15}{15}$ ° C.	0·9292–0·9374
Solidifying point	Semi-solid at 0° C.
Saponification value	187·4–190·3
Iodine value	115·0
Refractive index at 40° C. (Zeiss butyro-refracto-meter) . .	73·5

Hemp Oil.

Produced from the well-known hemp-seed (*Cannabis sativa*) which contains about 33—35 per cent. of oil. The colour is usually dark green, and the smell that of the seed.

We have obtained the following figures for one sample :

Specific gravity $\frac{15}{15}°$ C.	0·9283
Saponification value	191·0
Iodine value . .	161·7
Refractive index at $40°$ C. (Zeiss	
butyro-refractometer) .	73·5
Free fatty acids	2·3%

The iodine value, according to other observers, varies between 140·5—166·0 per cent.

The cake is used for feeding purposes. Analyses are given by Smetham (Analyst, 1910, vol. xxxv, p. 60, abs.).

Appendix A.

The   Disturbance   of   the   Reichert-Meissl-Polenske-Kirschner Value by the presence of Benzoic Acid.

It has recently been pointed out by Grimaldi (Annuli del Laboratorio Chemico. Centrale delle Gabelle, vol. vi, 1912, p. 631) that the use of benzoic acid as a preservative in butter and margarine has a decided effect on the above values.   The authors have investigated this and find that such an effect is produced, but that in the case of margarine considerable quantities are required to produce a marked disturbance of the correct values. The effect is practically limited to the Reichert-Meissl and Kirschner values, the Polenske value being unchanged.   In any case, the effect of the benzoic acid is completely removed by washing the fat with a solution of sodium *bicarbonate.*   For this purpose about 50 grm. of the melted fat are shaken *violently* for five minutes with 150 c.c. of a 5 per cent. solution of sodium *bicarbonate.*   After separation of the fat, it is washed once with about 150 c.c. of warm water and the fat is then filtered and rendered water-free in the usual way.

The authors have obtained the following figures which illustrate this :

Sample.	Reichert-Meissl.	Polenske.	Kirschner.
Margarine mixture . .	5·87	6·65	1·09
,, ,, + 0·5% benzoic acid	6·48	6·68	1·14
,, ,, after bicarbonate treatment	5·85	6·70	1·09
Mixture + 2% benzoic acid . .	7·59	6·72	1·36
,, after bicarbonate treatment	6·03	6·57	1·06

If, therefore, the presence of benzoic acid be detected in a margarine fat, it should be treated with sodium bicarbonate before determining the Reichert-Meissl-Polenske-Kirschner values.

It would appear from the original paper that the effect in the case of butter fat is greater than with margarine fats. As the use of benzoic acid as a preservative is likely to become extensive on the Continent in the near future, the above facts become of importance.

Appendix B.

A New Test for Soja Oil.

Settimj, in the above-mentioned journal, p. 461, proposes a new test for soja oil, in which 5 c.c. of the oil, 2 c.c. of chloroform and 3 c.c. of a 2 per cent. aqueous solution of uranium nitrate are shaken together, when soja oil produces an intense *lemon yellow* colour, which is not the case with other liquid oils. The test appears, however (as Settimj himself points out), to depend on the presence of an impurity, and the reaction, as the authors have determined, is not given by the *refined* oil.

Appendix C.

Hydrogenised Oils and Fats.

Comparatively recently a number of patents, too numerous to describe individually, have been taken out both in this country and abroad for the commercial treatment of fats and oils with hydrogen in the presence of a catalyst, with the object of converting liquid oils into solid fats and hardening fats which are already solid.

The *modus operandi* varies according to the different processes employed, but generally speaking the fat or oil is heated under pressure while being agitated in an atmosphere of hydrogen in the presence of various catalysts, such as palladium, nickel, copper, cobalt, etc., in a finely divided condition or with metallic salts. The unsaturated glycerides take up hydrogen to form saturated compounds of another series; thus in the case of olein, stearin is produced as follows:

$$C_3H_5 \ (O.C_{18}H_{33}O)_3 + 3H_2 = C_3H_5 \ (O.C_{18}H_{35}O)_3$$
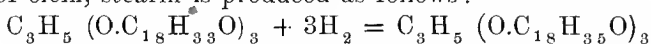
As a result of these inventions, it may be expected that sooner or later there will be no small quantity of hydrogenised fatty products on the market, and as factories are now being established for the preparation of these fats for edible purposes, the difficulties of the analyst in resolving the composition of mixtures of fats, or even in recognising a single oil so treated, will be very greatly increased.

Liquid oils become lard-like fats or even harder, and many of their characteristic reactions are lost; for example, hydrogenised cotton seed oil no longer responds to the Halphen or nitric acid tests.

The iodine value of fatty products so treated is reduced directly in proportion to the extent of hydrogenisation, and may fall from that of the original oil or fat to as low as 2 or 3 per cent. The refractive index is considerably lowered, but the reduction in the saponification value is, naturally, not appreciable.

The process is also applicable to the fatty acids themselves, but the consideration of this does not come within the scope of edible products.

CHAPTER VI.

RANCIDITY.

THERE is probably no question which so constantly
exercises the mind of the oil analyst as that of the
occurrence of rancidity, either in oils and fats them-
selves, or in products of which they form a constituent.
In the latter case it is quite usual for the manufacturer
to accuse the oil which is used as being the primary
cause, and in consequence blames the oil manufacturer
for want of care in the refining of his product.　It is
needless to say that such an accusation can scarcely
ever be substantiated conclusively, as, when mixed with
highly nutritive substances, the fat is completely at the
mercy of any lipase-producing organisms which may
happen to have gained access to the final product during
manufacture, and which will develop immediately their
environment becomes auspicious.　Needless to say,
however pure or highly refined an oil may be, such
attributes provide no protection to the fat, so that when
rancidity has appeared in such manufactured products,
as chocolate biscuits and confectionery in general, the
cause will be found with far greater likelihood in faulty
methods of manufacture, and, more particularly in the
case of confectionery, to an excessive moisture content
coupled with unsound constituents.

When all is said and done, rancidity is a " sen-
sation," in the greater number of cases, or rather

the "sensation" may be the only real evidence. From the state of being a "sensation" it may increase to such an extent that its presence becomes sensible to chemical tests. It is, however, too often forgotten that it is with the "sensation" stage that the chemist is generally asked to deal, and it is for this reason that the best tests for rancidity are still the tests of taste and smell, which are not the sole perquisite of the analyst. The progress of rancidity to that of evident chemical change is not always concurrent with that of the production of free fatty acids, and the absence of free fatty acidity is not a criterion of non-rancidity. In unrefined oils the two undoubtedly are generally concurrent, but in refined oils (from which the free fatty acids have been once removed) there may just develop a distinct "sensation" of rancidity, which will be followed later by the reproduction of free fatty acids.

The Causes of Rancidity.

These are many, and they are by no means properly understood. When rancidity is the product of age the factors are generally moisture, light and air, but when rapid development takes place in the case of a freshly prepared oil, the cause is more often the result of the activity of organised bodies such as moulds, and to a lesser extent, bacteria.

There are, however, cases of the rapid production of rancidity which must be ascribed to auto-oxidation, the process being started in some manner in the early stage of the oil's history (most probably if at any time it has been exposed to an elevated temperature), and proceeding afterwards catalytically in a manner not properly understood. In these cases it is noticeable that a strong

" sensation " of rancidity may develop long before the iodine value commences to fall.

In general practice, and particularly in the case of margarines, the production of rancidity can in most cases be ascribed to moulds. Not that moulds are capable of anything but the slightest development upon pure oils and fats, but that the packing of such oils and fats in wooden barrels for transport, or the admixture with milk constituents, as in the preparation of margarines, provides the necessary nidus for their growth, so that, finding themselves with the needful means of subsistence, they develop mycelia, which spread over or penetrate into the fatty material, and at the fruiting stage, or sometimes even before this, cause a rapid hydrolysis of the glycerides, with the consequent production of free fatty acids. In such cases the change can only be hindered or restrained by a suitable treatment of the wood in the one case, or an addition of preservative in the other, but in neither case does the fault lie with the fatty material *per se*, but with the conditions in which it has been placed, and these conditions have not always the same effect upon different fats and oils. In certain cases the actual amount of mould growth may be so small that it can only be detected by most careful examination, or its structure may have so far disintegrated as to be no longer recognisable, but the lipase secreted by it may continue its effect long after the original source has died out.

It is not improbable that *partial* oxidation of glycerine is the actual provocative agent of the rancid taste, and we may therefore have the case of the production of free fatty acidity, unaccompanied, at first, by the " sensation " of rancidity, if organisms be present which can, by their activity, bring about the rapid and

complete oxidation of the glycerine produced in the hydrolytic process.

From what we have already said, it will be seen that chemical tests for rancidity are of comparatively little value, for the " sensation " stage is not always sufficiently accentuated to allow corroboration by chemical tests, while, if the rancidity has progressed to any extent, the fact is so patent as to require no corroboration.

TESTS FOR RANCIDITY.

(1) In a test-tube mix equal volumes of the oil or fat (melted, if necessary, at the lowest temperature at which it will remain liquid) and Schiff's reagent. Cork and shake vigorously and allow to settle. In the presence of *some* forms of rancidity a *violet* colour, more or less intense, is produced either immediately or within a few minutes. The test, however, fails completely with such fats as butter fat and is much too delicate for coconut oil, in which a colour may be produced when there is not even the slightest " sensation " of rancidity.

Schiff's reagent may be prepared as follows : Dissolve 1 grm. of rosaniline in about 500 c.c. of water and add slowly 5 grm. of sodium bisulphite dissolved in water and 10 c.c. of concentrated hydrochloric acid, and make up to one litre. The solution should be quite colourless and will keep almost indefinitely in the dark.

(2) *Viedmann's reaction.*—Mix 5 c.c. of the oil or fat with 5 c.c. of a 1 per cent. acetone solution of phloroglucinol and add two or three drops of concentrated sulphuric acid. The production of a *red* colour is said to indicate the presence of rancidity, and according to Viedmann, an admixture of 1 per cent. of a rancid fat with normal fat may be detected.

(3) *Kreiss' reaction.*—According to this investigator, rancidity in oils and fats which has been brought about by long exposure to air, light and moisture, may be detected by shaking the oil with 1 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) and 1 c.c. of a 1 : 1000 ethereal solution of any hydroxybenzene which possesses two hydroxyl groups in the *meta* position. Under these conditions resorcinol or pyrogallol produce a *violet*, and phloroglucinol a *red* colour if rancidity be present.

CHAPTER VII.

COCOA, CHOCOLATE AND MILK CHOCOLATE.

THE analytical problems connected with these food products are the problems of the last few years.   They have arisen mainly out of improvements in the processes of manufacture, but as these processes do not come within the scope of this book, the reader is referred to such a work as Cocoa and Chocolate, by R. Whymper (J. & A. Churchill, 1912), if details be required.

Undoubtedly cocoa was originally made by grinding the whole bean, and if this process had only been adhered to the analyst would have been saved from many difficulties which have arisen as the consequences of departure from it.   The " shell " (or testa), which becomes somewhat detached from the " nib " (coty-ledons) during the process of roasting, was not originally separated, but ground together with the " nib."   As the result of attempts to make an improved cocoa, the " shell " was removed as much as possible by a decorticating process, and the " nib " alone was used for the production of cocoa.   From this time " shell " began to accumulate, and naturally an outlet was sought for it.   In appearance and taste, as well as in analytical features, " shell " bears a close resemblance to " nib," so that it was not long before it was bought up, ground, and added to cocoa, in quantities beyond those

19

in which it would naturally occur if the whole bean had been ground, enabling the manufacturer to produce a lower priced article, which rapidly began to compete with cocoa made from " nib " only.

Out of this procedure all the difficulties have arisen, as it is evident that a cocoa which contains more " shell " than could naturally be present must be looked upon as an unnatural product, and great ingenuity has been displayed by the manufacturer in so preparing " shell " that the addition is masked, thus rendering the task of the analyst in recognising the addition very difficult. In view of the history of cocoa manufacture, there really seems no reason why " shell " should not be permitted up to that percentage which would legitimately occur if the whole bean were ground, but since Ceylon beans contain only some 7 to 10 per cent. of shell, while those from Trinidad may run as high as 20 per cent. (and even in exceptional cases as high as 30 per cent.), there remains in the case of the former variety a very large margin for manipulation, for which the composition of the latter may be pleaded as an excuse.

As the present situation has not yet been complicated by the promulgation of an official standard, each individual analyst is at liberty to use his judgment in cases with which he may have to deal. So far the only important test case which has been brought has resulted in a magisterial decision allowing a mixture containing 18 per cent. of shell to pass as genuine cocoa, but it is certain that the fixing of any definite standard will result in exactly the same situation as has resulted from the setting of an official standard for water in butter and for non-fatty solids in milk, and, in fact, which will always result in the case of any natural product which shows wide variations in composition.

The methods which we have given for the analysis of cocoa are, we trust, the best that are available in our present state of knowledge, and, being fortified by the description of the " levigation " process as worked out by Mr. T. Macara, will, we hope, enable the analyst to do all that analysis can do as yet for the solution of this difficult problem. We have given no tables of analyses of cocoa, firstly, because the question has necessarily resolved itself into a dependence on mean figures for the composition of both "shell" and "nib," for which reason these mean figures have been given, together with the curves which show how they are applied; and secondly, because though great numbers of analyses of cocoa, etc., have been published, most of them were put forward before this question became acute, and the methods employed were often somewhat indifferent, and in many cases would not give figures comparable with those which would be obtained by the methods we have described. The mean figures which have been given are based on results obtained by these methods, and it would probably be better to make deductions from these average figures rather than from results obtained with methods of unknown technique. So long as cocoa, chocolate or milk chocolate is prepared from pure " nib," or that substance together with the necessary sugar and condensed milk, their analysis is comparatively simple, but with the enormous increase in the production of cheap, though perfectly wholesome varieties, in which additions of shell, starch, etc., form no inconsiderable percentage, the analytical difficulties have become very great, yet with care it is possible to arrive at fairly satisfactory results, if sufficient analytical investigation be made.

Such substances as nut-milk chocolate and chocolate

to which an addition of nitrogenous or medicinal sub-
stances have been made do not allow of any scheme of
analysis, and such substances must be dealt with on
their individual merits, calling rather for the exercise
of common-sense on the part of the actual analyst than
for any outside guidance.

Analysis of Cocoa.

The analysis of cocoa will probably be made in order
to determine the composition of the product and the
possible presence and amount of shell, and in such case
its proportion to nib.   It will also be necessary to
examine the sample microscopically for starch, and if
the addition of foreign starch be suspected, to proceed
to its estimation.   The estimation of fat is also impor-
tant, as well as the determination of the ash and its
general constituents.

For the proper examination of cocoa it is advisable
to make most of the following determinations .

(a) DETERMINED ON ORIGINAL SAMPLE.

(1) *Moisture.*

This may be found in most cocoas by drying 5 grm.
in a platinum dish in the water oven to constant
weight.   The weighing is facilitated in this case (as in
that of all hygroscopic powders) if the dish be provided
with a cover of aluminium foil, which is placed in the
oven beside the dish, and placed on it immediately
before removing the dish from the oven to the desic-
cator, the lid being kept on the dish during the process
of weighing.   It need hardly be pointed out that
platinum dishes should always be left in the desiccator
for the same time (say five to seven minutes) before

weighing. In the case of " Ship's Cocoa " the above
method will be satisfactory, but if a really accurate figure
be required, scrapings of the mass should be dried to
constant weight in the vacuum desiccator.

(2) *Nitrogen.*

By the Kjeldahl-Gunning method, as set forth under
" Feeding Stuffs " (p. 331), using 1·0 grm.

The estimation of nitrogen is most important, as the
careful examinations of Winton, Silverman and Bailey
show that the percentage of nitrogen in the nib to that
present in the shell is as 2 to 1, the mean percentage
in the fat-free dry nib being 5·05 per cent., while that
of the fat-free dry shell is 2·55 per cent. It must,
however, be carefully noted that while the variations
(as found by them) in nib were only from 4·7 to 5·4
per cent., the variations in the case of shell were
much greater, namely from 1·9 to 3·4 per cent., from
which it will be seen that the nitrogen figure is not
sufficient by itself to determine the proportions of shell
and nib.

(3) *Fat.*

In the case of very finely ground cocoa not more
than 2 grm. should be extracted. The method of
extraction is that described on p. 11, but re-grinding
is not usually necessary. It is, however, helpful in
some cases to dry the extraction tube and contents,
after about one hour's extraction, and then, after
breaking up the cocoa mass, to continue the process.
It will usually be found that the ether refuses to per-
colate quickly, in which case, when about one
inch of solvent has accumulated on the cocoa, the
source of heat should be removed and the solvent

allowed to pass through. When this has happened four or five times all fat will have been extracted.

Cases of substitution of the cocoa-butter in cocoa by other fats have come under the authors' notice, and it must not be forgotten that such substitution is quite possible to a considerable extent as a result of modern improvements in methods of removing fat. For the examination of cocoa-butter see p. 164.

There is no legal limit to the fat percentage, but the amount usually found at the present time is from 25 to 30 per cent. This is, however, chiefly the outcome of the practical considerations of pressing machinery and the production of a palatable and convenient food material.

There is a tendency at the moment (which is probably the outcome of the high price of cocoa-butter and greater efficiency of presses) to lower the fat content. As to whether this effects a more suitable or digestible food product we offer no opinion, but the pecuniary advantage to the manufacturer is evident, at the present market prices of cocoa-butter and cocoa.

(b) Determined on the Fat-free Dry Residue.

In order to prepare a sufficient quantity of fat-free dry material for examination, it will be necessary to extract from 5 to 10 grm. of the cocoa with petroleum ether, which may be conveniently accomplished in an apparatus similar to that described on p. 10, but having a wide tube of large capacity. On account of the fineness of the material, the extraction tube will rapidly fill with condensed solvent. When this has occurred the apparatus is raised out of the water-bath until the solvent has percolated, then lowered again, and the process repeated not less than five times, when

all fat will have been extracted. (A Soxhlet extractor is *most* inefficient for cocoa, as the mass is not continuously penetrated.) In those laboratories which possess a high speed centrifugal machine of large capacity, the extraction of fat may be rapidly accomplished by shaking up the cocoa with solvent, centrifugalising, pouring off the solvent through a filter, and repeating the process twice more, using always as much solvent as possible.

The extracted residue is, in either case, then dried to constant weight in a wide-mouthed weighing bottle, and on it the following determinations are made :

(1) *Cold Water Extract.*

Booth, Cribb and Richards point out that the cold water extract of the fat-free dry nib or shell is practically the same, and averages 24 per cent., though the authors consider 26–27 per cent. more accurate for nib. To make the determination, 2·5 grm. of the material are shaken in a 100 c.c. flask with about 60 c.c. of water and made up to the mark. This is allowed to stand for twenty-four hours, and then filtered *bright,* which can only be conveniently accomplished by *repeated* filtration through the same filter-paper, taking care to avoid evaporation ; 20 c.c. of the filtrate are then dried to constant weight. If the figure obtained varies notably from 24 per cent. explanation should be sought. Added starch lowers the figure, and sugar raises it.

(2) *Fibre.*

This is determined exactly as under "Feeding Stuffs," (p. 336) using 1·0 grm., and no difficulty will be experienced even with the finest cocoa when using the method there described. The determination is next in importance

to that of the nitrogen, as the mean percentage of the fibre (according to Winton and others) is in dry and fat-free nib 5·6 per cent., and in dry and fat-free shell 18·0 per cent. The variations, however, are very large, particularly in the case of shell. These observers give a maximum of 20·7 per cent. and a minimum of 13·7 per cent. For this reason the information given by this figure must be used with care in calculating shell.

(3) *Starch.*

The authors are of the opinion that the most correct way of estimating starch in cocoa is by the " diastase method " (for details see p. 336).

For this purpose either the residue of the 2·5 grm. used for the cold-water extract determination may be employed, or a fresh quantity of 2·5 (or 5 grm.) used.

With cocoa great difficulty will be found in the preliminary washing, particularly when the sample is very finely ground. This difficulty is avoided by the use of a large Buchner filter. The cocoa is rubbed up in a dish with 50 c.c. of 10 per cent. alcohol, and the filter, fitted with an accurately cut paper, is filled with water and suction applied. When only $\frac{1}{4}$ in. of water remains the cocoa is poured on and the dish rapidly washed out with more 10 per cent. alcohol. Washing is easily effected with the remainder of the dilute alcohol required, followed by strong alcohol. The filter-paper is then carefully removed, and, with the adherent cocoa, dropped into a 250 c.c. flask and any particles of cocoa left in the filter washed in with water, holding the funnel in a sloping position and turning it round during the process. The conversion of the starch is then continued exactly as given on p. 336. The cocoa may be entirely confined to the filter-paper if a glass cylinder be available which can be pressed on to the edges of

the filter-paper before pouring in the cocoa, as shown in Fig. 31. Winton and others give a mean value of 17 per cent. of starch in fat-free dry nib, and 4·25 per cent. in fat-free dry shell.

The polarimetric method of Ewers may be used (for details see p. 335), but the authors have experienced much difficulty in using the original process, both on account of the deep colour obtained, and also of the great slowness of filtration.
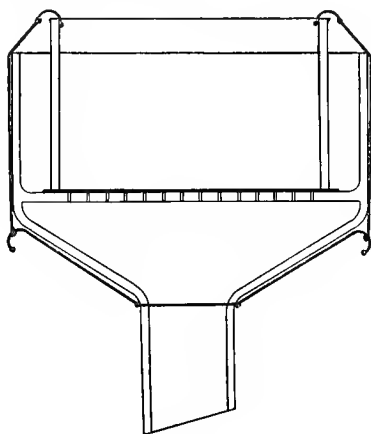
Fig. 31.

These difficulties are much diminished by the following modifications which they have devised :

2·5 grm. of the fat-free dry material are rubbed up in a dish with 10 c.c. of 50 per cent. acetic acid, and allowed to stand for a few minutes and filtered under pressure (preferably as above on a *small* Buchner filter). The dish is washed out with a further 10 c.c. of 50 per cent. acetic acid. This treatment removes most of the colour. The filter-paper and cocoa are then dropped

into a 50 c.c. flask, and the filter rinsed in with two lots of 12·5 c.c. of the required acid (HCl 1·124 per cent.) and the process continued as given on p. 335, taking care that *not more than* 5 c.c. of phosphotungstic acid solution are employed.

After filling to the mark, a slight addition must be made to compensate for the volume of filter-paper (which must be determined by the observer). The mixture will filter clear after the first two or three c.cs. have passed

The authors have found from 19 to 23 per cent. of starch in fat-free-dry nib and 9 to 10 per cent. in fat-free-dry shell, when using the polarimetric method as modified above.

(4) *Sugar*.

This is not often present, but if an estimation be desired, 5 grm. are shaken with 90 c.c. of water in a 100 c.c. flask, and the volume then made up to the mark ; 50 c.c. are filtered, and placed in a 100 c.c. flask and 0·8 grm. of pure citric acid added, and the flask heated in boiling water for thirty minutes and then cooled. The solution is diluted to about 90 c.c., and a few drops of basic lead acetate solution (see p. 310) are added till the precipitate settles out clear, and then 5 c.c. of a 10 per cent solution of crystallised sodium sulphate to remove any excess of lead, after which the solution is made up to the mark and filtered and the sugar determined by Fehling's method (p. 314). If much sugar be present it may be estimated as given under " Chocolate."

(5) *Phosphates*.

As phosphoric acid in some form appears to be present as added matter in some modern cocoas, it may be

necessary, in cases in which an excessive ash is found, to estimate the amount of P_2O_5. For this, the method given under feeding stuffs may be conveniently employed (p. 340).

(6) *Ash*.

The total ash merely forms a rough guide as to whether any mineral additions have been made. In cocoa prepared from the nib only, and untreated by alkali, the total ash does not exceed 6 per cent. calculated on the fat-free-dry material, but on the fat-free-dry shell it may be more than twice this amount, and varies over wide limits.

The soluble ash of the fat-free-dry nib does not exceed 4 per cent. and is but slightly higher for fat-free-dry shell. The colour of the ash is usually a greyish white ; any tendency to red may be due to iron.

The most important determination to be made on the ash, is that of the alkalinity, by which the presence of added alkali may be detected. This is estimated by titrating the water-soluble ash with $N/2$. HCl to methyl orange, and calculating as K_2O.

The alkalinity, so calculated, in cocoas untreated with alkali does not usually exceed 4 per cent., but as nearly all cocoas are treated with alkali it is quite usual to find an alkalinity of 5·0 per cent. and a total ash in consequence of 10 to 11 per cent. The alkalinity, as is pointed out later, may often be due to the use of lime or magnesium, and is not therefore necessarily soluble in water.

Probably the most elaborate investigation into the ash of cocoa has been made by Froehner and Lührig (Zeit. Untersuch. Nahr. Genussm. 1905, ix, p. 257 *et. seq.*), who also give two excellent methods for the esti-

mation of the total and soluble alkalinity, which are as follows :

Total alkalinity.—Five grm. of the cocoa are thoroughly carbonised and heated for one hour on the water-bath with 10 c.c. of $N/2$ H_2SO_4 and 25 c.c. of water, after which the excess of acid in the mixture is titrated with $N/2$ NaOH, using litmus paper as an indicator.

Soluble alkalinity.—The ash of 10 grm. of the cocoa is boiled up with 50 c.c. of water in a 100 c.c. flask for fifteen minutes, cooled, made up to the mark and filtered ; 50 c.c. of the filtrate are mixed with 5 c.c. of $N/2$ H_2SO_4 and the excess titrated with $N/2$ NaOH.

In either case the alkalinity is calculated as c.c. of normal acid per 100 grm. of dry cocoa matter, or as percentages of K_2CO_3 per 100 grm. of ash.

The following are some of the figures given by them, reckoned on the dry unextracted cocoa matter :

They find a *total ash* of 4·5 per cent. in nib from Ceylon and Maracaibo as a maximum, and 2·46 per cent. as a minimum in Bahia, giving 3·64 per cent. as a mean figure for a large number of cocoas. For the *alkalinity* of the *soluble* ash per 100 grm. of dry nib, they give limits of 5 to 20 c.c. of normal acid, with a mean figure of 11·5 c.c., and as *percentages of* K_2CO_3 per 100 parts of ash they give limits of 12·6 to 32·5 with a mean figure of 21·4. The following table gives their figures for certain kinds of cocoa :

Cocoa.	Alkalinity of soluble ash per 100 grm. of dry cocoa in c.cs. of normal acid.	K_2CO_3 per cent. per 100 parts of ash.
Maracaibo	20·0	32·5
Ceylon	18·7	28·6
Puerto Cabello	13·3	25·7
Java	13·1	25·3

Cocoa.		Alkalinity of soluble ash per 100 grm. of dry cocoa in c.cs. of normal acid.			K_2CO_3 per cent. per 100 parts of ash.
Accra .	.	10·4	.		20·4
Caracas		10·3	. '	.	17·7
Machala	.	9·3	.		17·2
Ariba .	.	.	9·0	.	.	16·0
Bahia .	.	.	7·0	.	.	15·5

In dry shell.—Lührig finds that the total ash soluble in HCl has a mean value of 6·46, but in certain cases it may be as high as 14·0. The alkalinity of the total ash per 100 grm. of dry shell in c.c. of normal acid has a mean value of 43·5, but the variations are wide, namely, from 22·5 to 64·5. The mean percentage of K_2CO_3 in 100 parts of the ash (soluble in HCl) is given as 46·6.

They point out that it is necessary to estimate the alkalinity both of the soluble and insoluble ash in order to detect added alkali, as magnesium carbonate is sometimes added instead of potassium carbonate. They give it as their opinion that a 3 per cent. addition of alkali will cause the soluble alkalinity of the ash of 100 grm. of the dry cocoa to exceed 74 c.c. of N/1 acid or the insoluble alkalinity to exceed 114 c.c.

(7) *Microscopical Examination.*

Much information may be obtained by this examination both as to the presence of shell and of foreign starches. A little of the fat-free dry material is placed in a drop of water on a microscope slide, and examined with a $\frac{1}{6}$-in. objective. The presence of shell is indicated by the presence of reddish-brown particles of varying size, and, if there be a notable proportion of shell, these particles will be found in every field, whereas in the case of the pure nib they will only be very sparsely scattered over the preparation.

The microscopical appearance of cocoa starch is very characteristic; the granules are practically circular, and have an average measurement of 0·0066 mm. They usually appear either singly or in groups of two or three granules. The hilum is usually indistinct and central, and with polarised light under a high power ($\frac{1}{12}$ in.) they show distinct brilliant crosses. The only starch with which it may be confused is that of the peanut (see Plate II), but the granules of this are distinctly larger, and when carefully compared other differences will be seen, which are sufficient to enable one to detect it with reasonable certainty. There are, however certain nuts and seeds (small consignments of which the authors have come across) which contain starches more closely akin to cocoa starch, but as these have not as yet come on the market in any quantity they need hardly trouble the analyst at present. If foreign starches are suspected they should be compared with the plates given, or with specimens of actual starches.

Certain skilful methods of manipulation effected by careful winnowing and grinding of the shell have made it possible to produce cocoas containing much larger percentages of shell than the foregoing chemical methods would indicate. Fortunately a mechanical method of arriving at the amount of shell is possible, which is not affected to any great extent by the chemical properties of the shell. For permission to publish the details of this process we are greatly indebted to Mr. Thomas Macara, who has made this "levigation" process both simple and exact. He has furnished us with the following account and details of the method, which in our hands has given most excellent results.

1
Cocoa
showing spiral
vessels.
× 150.

2
Cocoa
showing spiral
vessels.
× 150.

3
Cocoa +
wheat starch.
× 200.

4
Cocoa with
fragments of shell.
× 200.

5
Cocoa +
maize starch.
× 200.
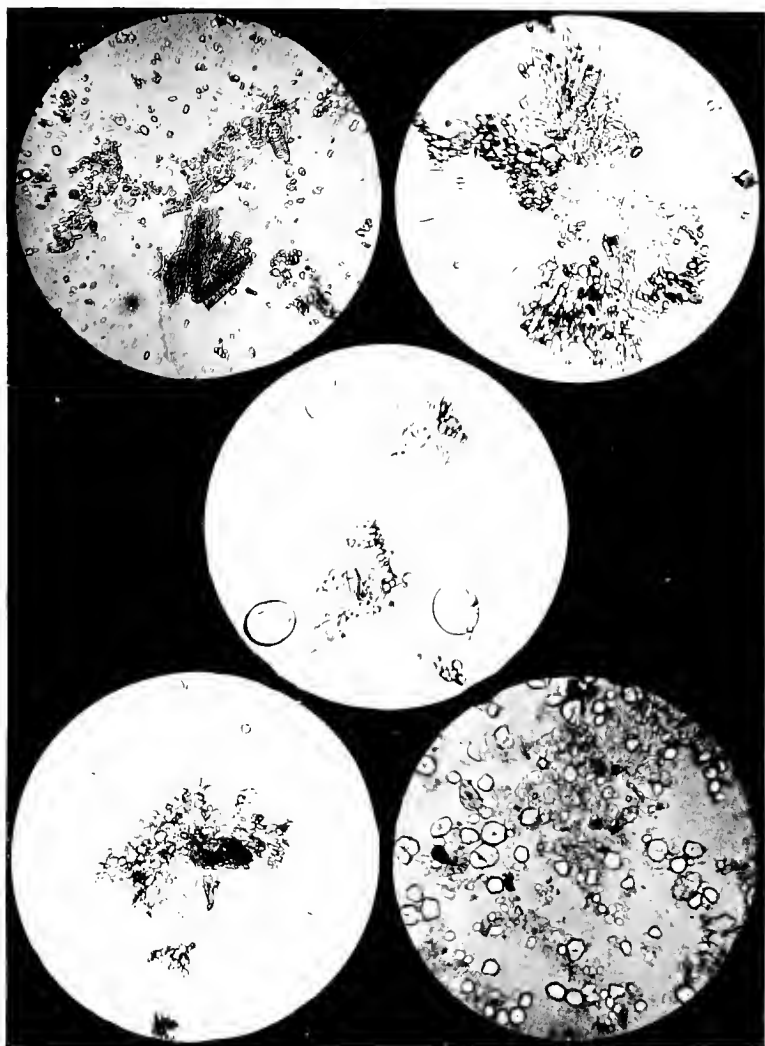
PLATE II.

COCOA.

KEY TO PLATE III.

1
Tapioca.
× 200.

2
Pea Nut,
showing starch granules.
× 150.

3
Tous le mois
× 200.

4
Wheat.
× 150.

5
Barley.
× 150

6
Ginger.
× 200.
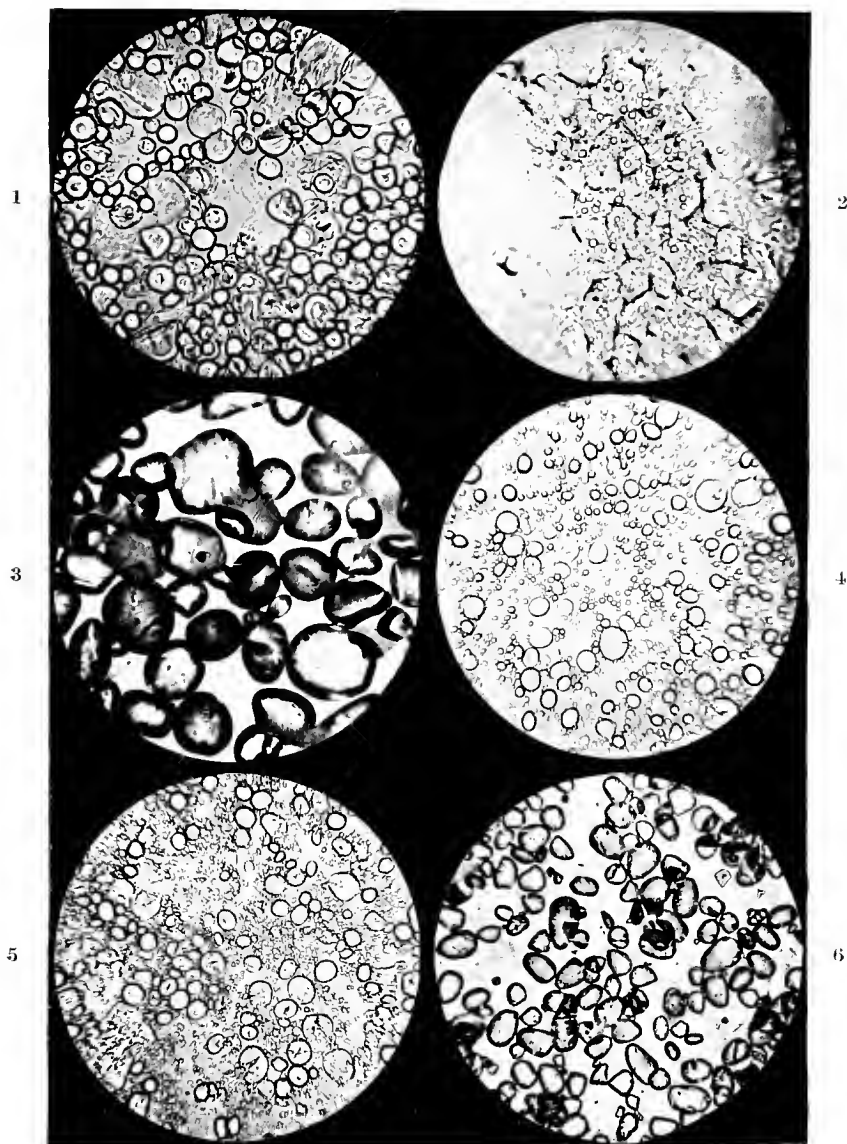
PLATE III.

STARCHES.

1
Rice.
× 150.

2
Rice + Arrowroot.
× 150.

3
Maize.
× 150.

4
Arrowroot
(Natal).
× 150.

5
Sago.
× 150

6
Potato.
× 150.

PLATE IV.
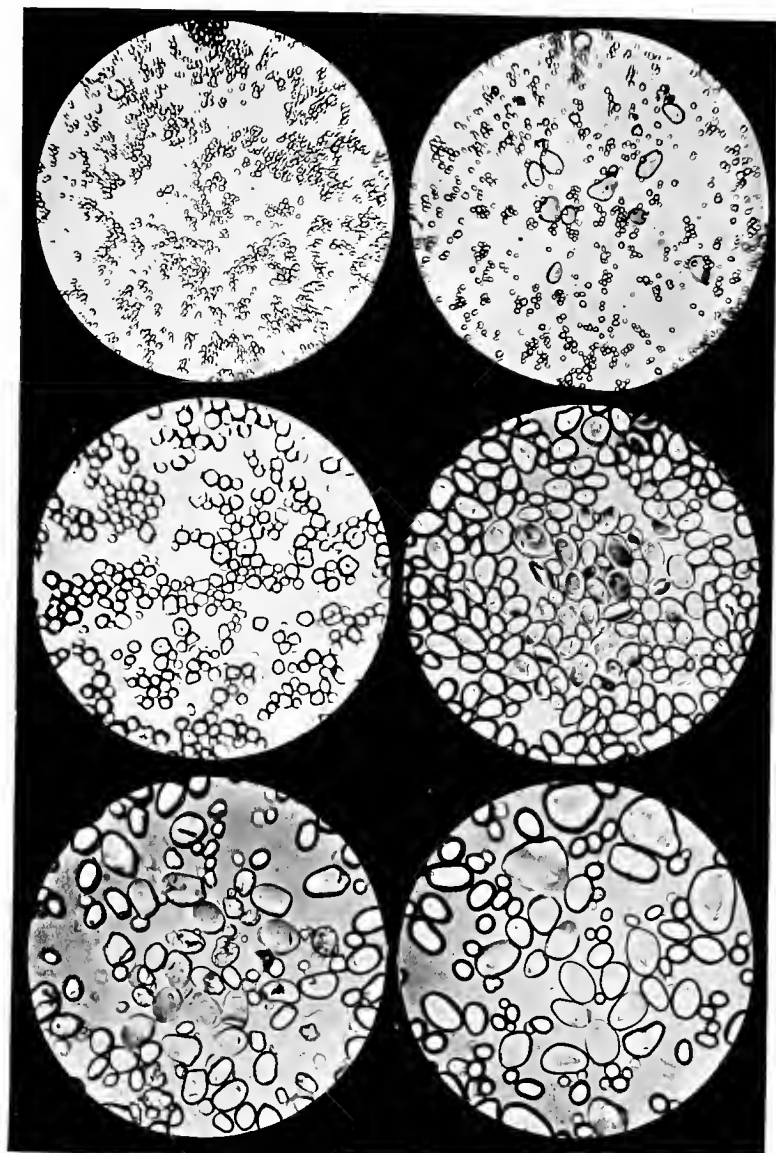
STARCHES.

"The Determination of Cocoa Shell in Cocoa Powders by a ' Levigation' Method.

" Many processes have been suggested for this purpose, but the only one which gives reasonably true and concordant results is a modification of the levigation method originally suggested by Filsinger in 1899. This process is based on the following differences in the physical properties of the cocoa nib and shell.

" (1) The whole nib is exceedingly difficult to grind to a fine condition, but when *completely* de-fatted can be reduced to an impalpable powder with the greatest ease.

" (2) The shell, both before and after de-fatting, cannot (in the dry condition) be ground to such a degree of fineness in a mortar in the ordinary manner.

" (3) When rubbed down with water, and the mass diluted, the cocoa nib material settles out of the liquid very slowly while the water-logged particles of shell, consisting chiefly of spiral vessels and sclerenchyma, deposit rapidly.

" The principal drawbacks to this process are, that besides the soluble portion of the shell, quite a large proportion of the shell-fibre is retained in suspension with the true cocoa material, and conversely some of the larger and heavier particles of the nib, more especially Mitscherlich particles and fragments of germ, settle out with the husk. Further, the percentage of husk recovered in this way will vary according to the nature of the shell (*i. e.* the variety of cocoa from which it was derived), and the degree of fineness to which it has been ground. It follows from the above facts that the process must in any case be an essentially empirical one to be worked out on very precise lines, in order to arrive at anything like concordant results, and

that these will only be absolutely correct if the nature, etc., of the shell employed be known, and the process standardised with mixtures containing known quantities of it. It will therefore be found advisable for each individual observer to standardise the process and apparatus for himself."

The following suggestions will enable most analysts to arrive at useful results :

Ten grm. of cocoa or chocolate powder should be thoroughly defatted in a continuous extraction apparatus, the process usually reqniring at least twelve hours' extraction, *as every trace of fat must be removed.* The residue, after the removal of the ether, is dried in the water oven and carefully ground in a porcelain mortar. Water is then added and the mass worked up into a thin cream, and finally diluted to 500 c.c. in a tall graduated cylinder. After standing for a fixed period, say fifteen minutes, the muddy supernatant liquid is run off by means of a syphon with a turned-up end to within a short distance of the sediment. The latter is shaken up with more water (to 500 c.c. mark), allowed to settle again for ten minutes, syphoned, and the process repeated, shortening each time the standing period nntil the supernatant liquid is quite clear after standing for five minutes. The residue should then be examined under the microscope, when the spiral vessels and sclerenchymatous cells of the shell can easily be recognised, as they are sufficiently transparent when distended with water. It will also be readily notice-able whether all cocoa, starch, etc., has been removed, and other cocoa material can also be recognised by its characteristic appearance. If the examination prove satisfactory (*i. e.* if 90 per cent. is recognisable as shell) the residue should then be transferred to a platinum capsule, dried and weighed. It should then be ignited

and any sand present estimated, this being deducted from the residue.

A pure cocoa should be treated in exactly the same manner, in order to arrive at the cocoa material left by the particular method adopted. In the same way the residue from pure shell should be determined. This latter figure will be from 25 to 35 per cent. of the original shell used. The necessary corrections and calculations are obvious. We have indicated on the curves the figures for shell and nib which we usually obtain, viz. for dry fat-free nib 3·0 per cent., and for dry fat-free shell 30 per cent.

The authors feel after experience of the process that Mr. Macara has hardly done justice to his method in the above description, as it not only exceeds in accuracy, but also in the amount of information given, any of the analytical methods which are possible.

Macara has designed a more elaborate method, using a continuous flow apparatus which allows of more exact results, but as it requires more standardisation the above method is recommended for casual use.

FIG. 32.

Percentage of components.

Percentage of N in fat-free Shell.
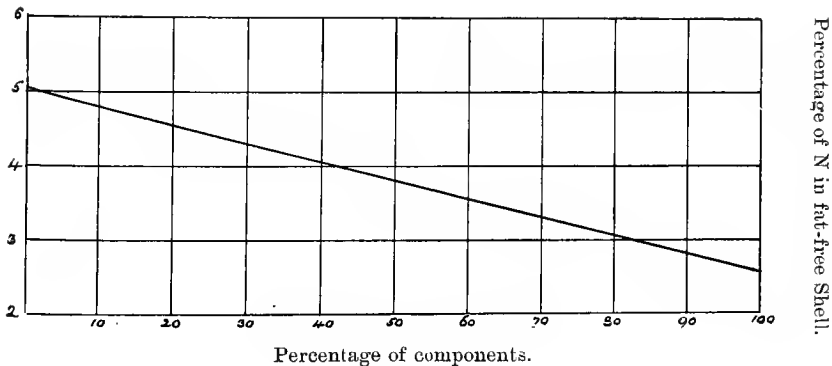
F𝜄ɢ. 33.
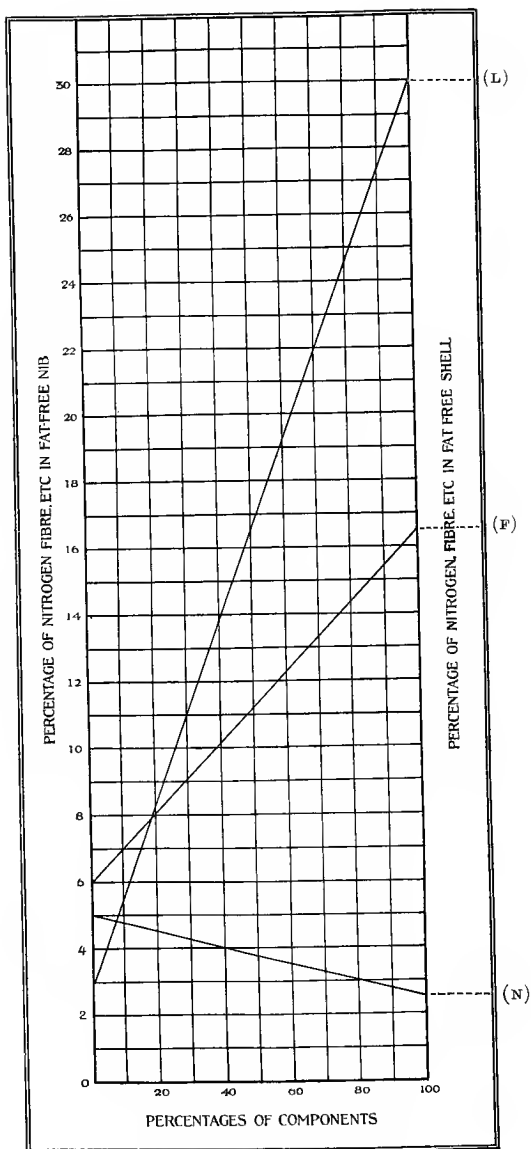
(L) = Levigation curve.

Calculation of Amount of Shell and Nib.

The accompanying curves will assist the analyst to determine approximately the proportion from the analytical figures obtained for the nitrogen and fibre in the fat-free-dry material, and more particularly from the results of the levigation process. They are based on a slight modification of the limits in the text. Fig. 32 is the nitrogen curve, on a larger scale for readier reading.

It is not to be expected that the various estimations will give the same proportion, and a mean should be taken, rather more reliance being placed on the nitrogen figures than on those of the fibre, and most certainty being allocated to the levigation results. The results so obtained are then calculated on the original sample.

The above assumes that there is nothing present but " cocoa-matter." If there be added starch, etc., the calculations are somewhat more complicated and the actual cocoa-matter present must be obtained from the cold water extract figure.

The methods of arriving at this in such cases are given under " Chocolate."

Chocolate.

As we have pointed out above, this substance will contain all the constituents of cocoa in varying proportions, and will also contain *cane-sugar*, and in many cases small quantities of *starches* other than those derived from the cocoa bean.

The methods of examination are practically those used in the analysis of cocoa. The determination of the cold water extract becomes of greater importance as furnishing the only basis from which the proportion of fat-free-dry cocoa matter may be calculated after

correcting it for the amount of sugar present, and, if there be any appreciable quantity of added starch, for the cold water extract of this starch. The following table, due to Booth, Cribb and Richards, gives the cold water extract and nitrogen figures for likely starches.

Flour.	Cold water extract.	Nitrogen.
Wheat	7·7	1·97
Barley	5·1	1·2
Maize (cornflour)	0·8	0·14
Rice	0·9	1·23
Sago	1·98	0·03
Arrowroot	0·4	0·13

In order to arrive at the amount of cocoa matter and the added starch in a chocolate the following method will be found of some advantage :

In the fat-free-dry sample the total nitrogen, total fibre, total starch, and total cold water extract are estimated, together with the amount of cane-sugar. The nature of the added starch is found from the microscopical examination, and the true values for the percentage of actual cocoa matter and added starch can then be found by applying the following equations :

In the fat-free-dry sample let—

X = percentage of true cocoa matter (required).

Y = percentage of added starch (required).

C = percentage of cold water extract of added starch (found from table).

T = percentage of total water extract in sample (determined and corrected for sugar only).

S_c = percentage of starch in cocoa matter.

S = percentage of total starch in sample (determined).

N = percentage of total nitrogen in sample (determined).

N_s = percentage of nitrogen in added starch (found from table).

$F =$ percentage of fibre in sample (determined).

Then assuming an approximate value of 10 for the value S_c.

$$X = 100 \left(\frac{100\ T - C.S.}{2400\ -\ S_c.C} \right),$$

$$\text{and } Y = 100 \left(\frac{24\ S - T.S_c}{2400 - S_c.C} \right).$$

Or, if no assumption of S_c be desired, then—

$$Y = 100 \left(\frac{T - 3.73\ N - 0.89\ F}{C - 3.73\ N_s} \right),$$

$$\text{and } X = \frac{100\ T. - C.Y}{24},$$

assuming in the above equations that fat-free-dry " nib " contains 5 per cent. of nitrogen and 6 per cent. of fibre, and that fat-free-dry " shell " contains 2·5 per cent. of nitrogen and 16·5 per cent. of fibre. The actual percentage of nitrogen in the cocoa matter (X) may now be determined by subtracting that due to the added starch (Y), whence from the fibre and nitrogen values of the cocoa matter the relative proportions of nib and shell may be found from the curves given on pp. 305–6, and the result should be in substantial agreement with the figures obtained from the levigation process. All values are then calculated to the original sample.*

The corrections for nitrogen and cold water extract are only necessary when wheat or barley starches are present. The methods of analysis are, as stated, similar to those of cocoa, with some slight modifications :

The sample should be scraped or shredded with a knife.

Determinations of *moisture, nitrogen, fat* and *cold water extract* are exactly the same as in the case of

* For example of method of calculating results, see Appendix D (p. 362).

cocoa. For *fibre* 1·5 grm. should be used. For the *starch* 5 grm. are used, and care must be taken that all cane-sugar is removed by washing. When the polarimetric method is employed, this may be subsequent to the acetic acid treatment. Washing is quite simple if the large Buchner filter be used.

For estimation of the *sugar* two separate quantities of a quarter and half the normal weight of the fat-free-dry material are dissolved in 100 c.c. of water, and cleared after filling to the mark with solid basic lead acetate (0·1–0·3 grm.), or by the addition of 5 c.c. of *plumbi subacetatis liquor B.P.* (see below) and 5 c.c. of alumina cream, allowing, in the latter method, for the dilution. Multiply each reading by two, when the *true* reading (= percentage of sugar in fat-free-dry material) equals the product of the readings divided by their difference. For Ventzke scales 6·512 grm. and 13·024 grm. will be employed, and the *true* reading (if in saccharimeter degrees) is direct percentage of sugar (angular degrees × 28·82 = saccharimeter degrees).

If Fehling's method (p. 314) be employed a 2·5 per cent. solution of the chocolate should be made, and no correction for the volume of the cocoa matter is necessary. The procedure is that given under " Cocoa " (p. 298).

Preparation of Basic Lead Acetate Solution.

If the B.P. preparation be not available, the solution may be made by boiling 430 grm. of normal lead acetate and 130 grm. of recently ignited litharge with 1000 c.c. of water. After cooling and settling the clear liquid is syphoned off, and diluted to sp. gr. 1·25.

Alumina cream may be made by adding ammonia to a strong solution of alum till there is only a slight excess of the alum left.

Milk Chocolate.

The analysis of milk chocolate presents greater difficulties than that of plain chocolate, and becomes very complicated when both nib, shell and foreign starch are present. We think it advisable to deduce the amount of milk-solids present from an accurate determination of the lactose in the fat-free-dry sample, confirming the percentage of milk-solids so obtained by an estimation of the actual ₊casein present. The non-fatty solids present in the mixture due to the original milk employed can then be calculated on the very fair assumption that, of the non-fatty solids of that milk, thirteen twenty-fourths are anhydrous lactose and eight twenty-fourths are casein. The total milk solids in the fat-free-dry sample so deduced are subtracted from the total solid matter of the fat-free-dry sample, when the remainder will be cocoa matter plus foreign starch plus cane sugar.

The cane-sugar is determined at the same time as the lactose by the method to be described, when the mixture left will resolve itself into cocoa-matter and foreign starch, the relative proportions of which may be determined as already described under " Cocoa." That is to say, (a) the total starch by diastase or Ewers' method, after washing out the cane-sugar, (b) the total nitrogen in the original fat-free-dry sample corrected for the nitrogen due to the milk proteins (the amount of which will have been already arrived at), (c) the total fibre, which may be estimated on the original fat-free-dry sample, and (d) the proportion of shell by the levigation process. These various determinations being made, the formulæ given under "Cocoa" are applied and the percentage of shell, nib and added starch will then be arrived at.

It will, however, be obvious that, except in the case

of milk chocolate made from pure nib, dried or con-
densed milk and cane-sugar, the analysis is beset with
difficulty on account of the wide variations in the com-
position of the various constituents and the relatively
small proportion in which some of them may be present.
The investigation has, therefore, rather the character of
a scientific than of a technical analysis, but the appli-
cation of care in the analytical details and of common-
sense in their interpretation will in most cases lead to
satisfactory results.

The following are the special methods of analysis
connected with milk chocolate.

Cane and Milk Sugars.

Ten grm. of the fat-free-dry residue are placed in
a 100 c.c. flask, dissolved by shaking with 70 c.c. of
water, and 15 c.c. of acid mercuric nitrate solution
carefully run in, allowing the liquids to mix as little as
possible.   The contents are adjusted to the mark with
water quickly and without disturbance, and then rapidly
and thoroughly mixed by vigorous shaking.   The con-
tents of the flask are cooled to about $10°$ C. (in order to
avoid incipient inversion of the cane-sugar by the acid
mercuric nitrate) and then filtered at this temperature,
and a direct polarisation made at room temperature as
quickly as possible.

Fifty c.c. of the filtrate are placed in a small flask,
and counterpoised.   The flask is then heated in boiling
water for *seven* minutes (evaporation being avoided as
much as possible), cooled, re-adjusted to the original
weight, filtered if necessary and polarised at the *same
temperature* (t) as that of the direct polarisation.

In order to allow for the bulk of the precipitate
produced by the mercuric nitrate, an exactly similar

experiment is carried out using 5 grm. of the sample. From the readings obtained in the two experiments the true values are found in the following manner :

If R_1 is the reading of the 5 grm. dilution, and R_2 is the reading of the 10 grm. dilution, then the *true reading for the* 10 *grm. dilution* is given by the formula, $R = \dfrac{R_2\ R_1}{R_2 - R_1}$ both for direct and invert readings.

The *true* reading having been thus obtained, the percentages of cane-sugar and lactose are calculated in the following manner :

(a) For instruments using the Soleil Ventzke scale :

Cane sugar per cent. $= \dfrac{(D-I)\ 100}{142\cdot68 - \dfrac{t}{2}} \times \dfrac{N}{W} = S$ and

Lactose per cent. (anhydrous) $= \dfrac{\left\{ D - S\left(\dfrac{W}{N}\right) \right\}\ 0\cdot31213}{W} \times 100 ;$

where D and $I =$ the *true* direct and invert readings
        for the 10 *grm. dilution,*

  $N =$ the normal weight for the instrument,

  $W =$ the weight of sample employed (*i.e.* 10 *grm.*).

(b) For instruments reading in angular degrees :

The reading due to cane-sugar $= \dfrac{21\cdot7\ (D-I)}{31\cdot31 - 0\cdot11t} = X$

(Tuchsmidt's formula),

then $D - X =$ reading due to lactose.

And as 1 grm. of cane-sugar dissolved in 100 Möhr c.c. gives a reading of $1\cdot33$ angular degrees, then—

  $\dfrac{X \times W}{1\cdot33} =$ percentage of cane-sugar in sample ;

and since 1 grm. of lactose monohydrate dissolved in 100 Möhr c.c. gives a reading of $1\cdot058$ angular degrees, then—

$$\frac{(D-X) \times W}{1 \cdot 058} == \text{percentage of lactose monohydrate in the sample,}$$

which result must be divided by 1·053 to get *anhydrous lactose* per cent.

It may not be out of place to remind the observer that if I be negative, then $-I$ in the above formula is positive.

If a polarimeter be not available, the sugars may be estimated by Fehling's method:

For this purpose 5 grm. of the fat-free-dry sample are dissolved in water and made up to 100 c.c.; 25 c.c. are inverted by citric acid (see "Cocoa," p. 298), cleared with basic lead acetate and sodium sulphate, and used for the determination of the lactose and inverted cane-sugar after making up to 50 c.c. Fifty c.c. of the remainder are cleared in the same way and made up to 100 c.c. and used for the estimation of the lactose. The solutions in each case are filtered, the filtrates being suitably diluted before titration if necessary. The sugars are determined against Fehling's solution in the following manner (Ling's method, using Harrison's indicator):

Solutions required:

(a) *Copper sulphate solution.*—69·278 grm. of pure crystallised copper sulphate are dissolved in water and made up to 1 litre.

(b) *Alkaline tartrate solution.*—346 grm. of Rochelle salts are dissolved in hot water and mixed with 142 grm. of caustic soda, previously dissolved in water, the whole being cooled and made up to 1 litre.

(c) *Indicator.*—5 grm. of pure potassium iodide are dissolved in about 40 c.c. of water. To this are added 0·05 grm. of soluble starch, which has been dissolved in about 5 c.c. of water by boiling and cooled, the whole being then made up to 50 c.c.

A 10 per cent. solution of acetic acid is also required.

Method of analysis.—On a white porcelain tile place a series of mixtures of two drops of the starch solution and one drop of the 10 per cent. acetic acid. A number of pieces of quill tubing about 8 in. long and about $\frac{1}{8}$ in. in diameter are placed ready to hand.

20 c.c. of the copper sulphate solution are then measured *accurately* into a flask and mixed with 20 c.c. of the alkaline tartrate solution. Of this mixture 10 c.c. are *accurately* measured into a 200 c.c. Jena flask, and brought to the boil. The sugar solution is now run in from a burette (2 c.c. at a time), boiling between each addition until the blue colour has nearly disappeared. A drop of the solution is now removed by one of the quill tubes and mixed with the indicator on the tile. (No filtration is necessary, and a fresh tube should be used for each test.) The sugar solution is then added 0·5 c.c. at a time, testing after each addition, until *no* colour is produced in the indicator after the lapse of at least a minute. The experiment is then repeated, running in the sugar solution as before down to the point which last produced a colour in the first experiment, and then by successive additions of 0·2 c.c. until the " no colour " point is again obtained.

The number of c.c. of the sugar solution required in this last titration is read off and the lactose calculated as follows : Since 10 c.c. of the Fehling solution are reduced by 0·067 grm. of lactose monohydrate, then if X c.c. of the sugar solution are required :

$$\text{Percentage of anhydrous lactose in the original sample} = \frac{0\cdot067 \times 100 \times 40}{X \times 1\cdot053}$$

since 100 c.c. of the sugar solution contains 2·5 grm· of the original fat-free dry chocolate. If the sugar solution has to be further diluted the factor 40 must be proportionately increased.

The original filtrate of the chocolate would in most cases give the right concentration for the above determination, though if less than 20 c.c. be required to reduce 10 c.c. of Fehling it should be suitably diluted until about 20 c.c. are required for that purpose.

That portion of the filtrate which has been inverted with the citric acid should now be diluted until about 25 c.c. are required to reduce 10 c.c. of the mixed Fehling. (A rough experiment is made to determine the necessary dilution.)

The total sugars from the latter titration are calculated *as lactose* in an exactly similar manner, allowing for the extra dilution employed. The percentage of *real lactose* is subtracted from the percentage of *apparent total lactose* so obtained, and the difference multiplied by 0·709 will give the percentage of cane-sugar.

For general purposes it may be taken that 10 c.c. of mixed Fehling solution is reduced by 0·05 grm. of pure dextrose. In practice, however, it is not really sufficient to rely on this, and the Fehling solution should be set against pure dextrose, but as this is not easily obtainable it is practically always standardised against a solution of invert sugar of such a strength that the quantity of invert sugar required to reduce 10 c.c. of the mixed Fehling solution is contained in about 25 c.c. The following method of making this invert sugar solution and the tables from which the amount of dextrose or invert sugar in each 100 c.c. of the test solution can be ascertained are given by Ling and Rendle (Analyst, 1905, vol. xxx, p. 185) and Ling and Jones (*ibid.*, 1908, vol. xxxiii, p. 165).

Pure sucrose (0·95 grm.) is dissolved in water (150 c.c.) and boiled with $N/2$ hydrochloric acid (30 c.c.), the mixture being maintained in ebullition for one minute, cooled, neutralised by the addition of $N/2$ sodium

hydroxide (30 c.c.), and made up with water to 500 c.c. This solution contains 0·2 grm. of invert sugar per 100 c.c.

Volume of solution required by 10 c.c. Fehling's solution.	Dextrose in 100 c.c. of solution.	Invert sugar in 100 c.c. of solution.
c.c.	Grm.	Grm.
20	0·2427	—
21	0·2332	0·2412
22	0·2226	0·2311
23	0·2138	0·2218
24	0·2056	0·2132
25	0·1981	0·2052
26	0·1911	0·1980
27	0·1846	0·1910
28	0·1784	0·1846
29	0·1728	0·1787
30	0·1675	0·1731
31	0·1625	0·1678
32	0·1577	0·1629
33	0·1532	0·1583
34	0·1490	0·1539
35	0·1450	0·1497
36	0·1412	0·1458
37	0·1377	0·1421
38	0·1343	0·1385
39	0·1310	0·1349
40	0·1279	0·1319
41	—	0·1288
42	—	0·1259

It is also advisable to standardise the Fehling solution against pure lactose, for which purpose a water solution of the pure substance should be evaporated to dryness when the sugar is obtained in the anhydrous condition.

Casein.

The authors have employed a method of estimating the casein in milk chocolate based on its solubility in sodium oxalate or citrate. As, however, the method has been published in a somewhat improved form by

Baier and Neumann (Zeit. Untersuch. Nahr. Genussm., 1909, xviii, p. 13), their method is here described :

Ten grm. of the fat-free-dry chocolate are rubbed up in a mortar with a small quantity of 1 per cent. sodium oxalate solution, the paste washed into a 250 c.c. flask with about 200 c.c. of the oxalate solution, the whole heated to boiling and the flask filled nearly to the mark with hot sodium oxalate solution. The mixture is allowed to stand for eighteen hours, shaken occasionally, and is then filled to the mark with cold oxalate solution, mixed and filtered. To 100 c.c. of the filtrate are added 5 c.c. of uranium acetate solution, and then 30 per cent. acetic acid solution is dropped in slowly till the casein commences to precipitate. Five drops more of the acetic acid are then added and the precipitate separated, preferably by sedimentation or centrifugalisation (as it filters slowly) or on a Buchner filter (p. 297), and washed with a solution containing 5 grms. of uranium acetate and 3 c.c. of 30 per cent. acetic acid per 100 c.c. till the washings are free from oxalate. The filter and precipitate is dropped into a flask and the nitrogen is then estimated by Kjeldahl's process, using the factor 6·39 to calculate the nitrogen to casein.

CHAPTER VIII.

FEEDING STUFFS.

THE analysis of feeding stuffs is carried out in a somewhat arbitrary manner, the various constituents being classed together under certain headings, without, as a rule, any differentiation being made among the various substances present which are included under these headings. The headings under which the constituents of feeding-stuffs are almost universally returned are *moisture, ash, total protein (albuminoids), fat, digestible carbohydrates, and crude fibre.*

This method of return does not give a real idea of the true feeding value of the substance analysed. For instance, there is no discrimination between the various nitrogenous bodies present (and on which the food value of the material largely depends), nor is any idea given of the actual *availability* of the constituents. This is a very great drawback to the value of such analyses, but custom has attached to them an importance which will probably continue to be held.

The actual availability of the various constituents can only be ascertained by proper digestion experiments carried out on animals, from the results of which *factors of digestibility* for each important class of constituents of a very large number of well-known feeding stuffs have been calculated. From the analytical figures of a feeding stuff and its digestibility co-efficients, it is

possible to ascertain the relative amounts of various food materials which will make up a satisfactory *ration* for animals under various conditions. The bases of these calculations are the so-called *standard rations*, and though the value of these standard rations has often been called in question, there is no doubt that under unknown conditions they furnish a valuable basis for experimental rations, both to the analyst and the stockman. A brief explanation of the method of using these standard rations is here given, and though while we would warn the analyst against calculating strict rations for animals unless he has had practical experience of the subject, there is no reason why he should not be able to give guidance to the stock-keeper as to a satisfactory experimental ration, given the available feeding stuffs.

For the purpose of calculating rations, feeding stuffs are divided into two classes :

(*a*) *Roughage*, under which heading are included those feeding stuffs which provide bulk, such as hay, straw, grasses, silage, roots, etc.

(*b*) *Concentrates*, under which heading are included such feeding stuffs as contain various nutrient materials, particularly protein and fat, in relatively large proportions.

By the careful adjustment of these two classes of feeds, satisfactory rations of a most variable character which will fit in with available feeding stuffs can be made. There are various types of standard rations and of methods of arriving at the mixtures which will satisfy these. Some, however, are unnecessarily complicated, and the method here given is that chiefly used in America, and is based on what are known as the " Wolff-Lehmann " rations, and has proved both satisfactory in result and easy in calculation. For full details

Animal.	lb. per day per 1000 lb. live weight.				
	Dry Matter.	Digestible nutrients.			Nutritive ratio, $1 : \rightarrow$
		Protein.	Digestible carbo-hydrates.	Oil.	
Oxen—					
At rest	18	0·7	8·0	0·1	11·8
Medium work	25	2·0	11·5	0·5	6·5
Fattening cattle—					
1st period	30	2·5	15·0	0·5	6·5
2nd period	30	3·0	14·5	0·7	5·4
3rd period	26	2·7	15·0	0·7	6·2
Milch cows—					
Giving 16·6 lb. of milk	27	2·0	11·0	0·4	6·0
Giving 22 lb. of milk	29	2·5	13·0	0·5	5·7
Horses—					
Light work	20	1·5	9·5	0·4	7·0
Medium work	24	2·0	11·0	0·6	6·2
Heavy work	26	2·5	13·3	0·8	6·0
Growing cattle— Dairy breeds.					
Age in months. — Average live weight in lb.					
2– 3 . 150	23	4·0	13·0	2·0	4·5
3– 6 . 300	24	3·0	12·8	1·0	5·1
6–12 . 500	27	2·0	12·5	0·5	6·8
12–18 . 700	26	1·8	12·5	0·4	7·5
18–24 . 900	26	1·5	12·0	0·3	8·5
Beef breeds.					
2– 3 . 160	23	4·2	13·0	2·0	4·2
3– 6 . 330	24	3·5	12·8	1·5	4·7
6–12 . 550	25	2·5	13·2	0·7	6·0
12–18 . 750	24	2·0	12·5	0·5	6·8
18–24 . 950	24	1·8	12·0	0·4	7·2

of this method and the tables connected with it, reference should be made to the works of Henry (Feeds and Feeding, 1898) or of Armsby (Manual of Cattle Feeding : Wiley, New York.)

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The table on p. 321 gives a selection of the Wolff-Lehmann standard rations in certain particular instances.

These standards are for animals under normal conditions, and are to be used as *guides* only. The figures given under " dry matter " may be allowed to vary quite 10 or 12 per cent. if necessary. If animals are below normal size, it may be necessary to increase the nitrogenous nutrients by 0·3 lb. and the non-nitrogenous nutrients by 1·5 lb. per day per 1000 lb. of live weight.

In the case of the standards for growing animals, allowance is made for a moderate amount of exercise ; if *no exercise* be given the figures are to be reduced 15 per cent., or if *much exercise* be given they are to be increased by 15 per cent. The " *nutritive ratio*," which is the ratio of the amount of digestible carbohydrates and oil to the amount of digestible protein, is calculated as follows :

" The percentage of oil is multiplied by 2·4 (to make its heat value similar to that of the carbohydrates) and the product added to the percentage of digestible carbohydrates, the sum being then divided by the percentage of digestible protein." For instance, if a feeding stuff contains 10·2 per cent. digestible protein, 69·2 per cent. digestible carbohydrates, and 1·7 per cent. of oil, then the nutritive ratio equals—

$$\frac{(1·7 \times 2·4) + 69·2}{10·2.} = 7·2,$$ and is expressed as—

nutritive ratio = 1 : 7·2.

If the nutritive ratio be high it is said to be " wide," and implies a large excess of carbohydrates over protein, but if the ratio be very small it is said to be " narrow," and points to a protein content practically equal to that of fat and carbohydrates combined.

The value of the feeding stuff is sometimes expressed in " *food units*," which are calculated as follows :

The content of oil and albuminoids[1] are added and multiplied by 2·5, and to the product is added the content of digestible carbohydrates, the result being "food units."

The method of calculating rations is as follows :

The analytical figures for various kinds of feeding stuffs being ascertained, it is necessary to know the factors which represent the average digestibility of these constituents, which factors have been ascertained by digestion trials. The various constituents are then multiplied by the corresponding factor, when the composition of the feeding stuff in percentages of digestible nutrients is obtained. A selection of the available foodstuffs being made, they are combined in such proportions as shall give a composition corresponding as nearly as possible to that of the particular standard ration required.

The following example will show the method of carrying this out :

"It is required to provide a ration for a cow giving 22 lb. of milk per day, hay being available as roughage and flaked maize as a concentrate, together with oil-cake and some product such as middlings or offal, which are generally necessary to provide against constipation." On reference to the tables below (p. 325), the following analytical figures will be found for these substances.

Feeding stuff.	Dry matter.	Protein.	Digestible carbohydrates.	Oil.
Hay	85·7	9·3	41·3	1·5
Flaked maize	93·7	10·6	81·6	0·9
Middlings	88·2	13·1	58·9	3·3

Digestibility Co-efficients.

Hay	57	64	53
Flaked maize	84	85	90
Middlings	82	85	85

[1] This word is still used commercially instead of total protein.

Digestible Nutrients calculated from above.

Hay	5·3	26·4	0·8
Flaked maize	8·9	69·5	0·8
Middlings	10·7	50·0	2·8

As not more than 2 lb. of middlings can be given per day on account of their purgative properties, a tentative ration of say 20 lb. of hay, 8 lb. of flaked maize and 2 lb. of middlings may be made up. The values of these are obtained from the above figures as follows :

In 20 lb. of hay there are :

Dry matter $\qquad 85·7 \times \dfrac{20}{100} = 17·1.$

Digestible protein $\qquad 5·3 \times \dfrac{20}{100} = 1·06.$

Digestible carbohydrates $\quad 26·4 \times \dfrac{20}{100} = 5·3.$

Oil $\qquad 0·8 \times \dfrac{20}{100} = 0·16.$

The values for the maize and middlings being calculated in a similar way, the value of the ration is given as follows :

Tentative ration.	Dry matter.	Digestible nutrients.		
		Protein.	Carbohydrates.	Oil.
20 lb. hay.	17·1	1·06	5·3	0·16
8 lb. flaked maize	7 5	0·71	5·6	0·06
2 lb. middlings	1·8	0·21	1·0	0·05
	26·4	1·98	11·9	0·27
Standard ration	29·0	2·5	13·0	0·5

It will be seen that the ration falls short in each particular but principally in protein and oil, and this must be corrected by the addition of a foodstuff rich in these such as oil-cake, which will not increase the carbohydrates unduly at the same time.

Linseed cake will meet these requirements, and from the figures for this foodstuff, given in the table below, the change brought about by adding 3 lb. of linseed cake may be ascertained.

Feeding stuff.	Percentage composition.				Digestibility co-efficients.		
	Dry matter.	Protein.	Carbo-hydrates.	Oil.	Protein.	Carbo-hydrates.	Oil.
Concentrates :							
Corn cob meal	88·95	2·00	56·18	0·80	52	88	84
Flaked maize	93·70	10·62	81·56	0·87	84	85	90
Bran	88·55	16·46	57·01	4·33	79	69	68
Wheat middlings	88·20	13·10	58·90	3·30	82	85	85
Barley	85·05	8·59	67·96	1·46	70	92	89
Brewers' grains (dried)	89·99	19·50	42·31	6·93	79	59	91
Crushed oats	86·55	11·12	56·92	6·77	78	76	83
Rice meal	90·05	13·94	48·95	10·43	63	86	85
Linseed cake	88·84	29·50	35·54	9·50	85	84	93
Cotton-seed cake (decorticated)	91·00	43·78	23·56	11·38	88	64	93
Pea meal	86·30	24·87	52·97	1·86	83	94	55
Soya bean meal	96·15	43·25	30·77	11·33	87	73	85
Roughage :							
Meadow hay	85·70	9·32	41·28	1·48	57	64	53
Wheat straw	86·19	2·96	30·29	1·47	11	38	31
Oat straw	84·85	4·04	38·47	1·52	30	44	33
Barley straw	85·35	3·25	35·35	1·45	20	54	42
Clover hay	83·32	11·75	37·39	0·86	55	64	53
Mangolds	12·11	1·32	8·63	0·17	76	93	—
Turnips	8·15	1·05	5·25	0·20	90	97	98

The following table gives the figures for a few well-known oil cakes, the figures on the left being the analytical composition, and on the right the actual percentage of digestible nutrients. (The figures given are not of the same samples.)

		Percentage composition.			Authority.	Digestible nutrients %			Authority.
	Dry Matter.	Protein.	Carbo-hydrates.	Oil.		Protein.	Carbo-hydrates.	Oil.	
Maize germ cake	90·53	20·36	46·13	12·23	Bolton and Revis	9·0	61·2	6·2	Henry.
Cotton seed cake (decorticated)	90·42	41·87	24·42	7·11	,, ,,	37·2	16·9	12·2	,,
Coconut cake	87·8	19·25	42·8	8·30	,, ,,	15·6	38·3	10·5	,,
Palm kernel cake	86·5	16·8	—	10·10	,, ,,	16·0	52·6	9·0	,,
Sunflower cake	92·90	19·01	28·93	7·43	Smetham				
Pea nut meal (decorticated)	89·3	45·12	30·49	5·81	Bolton and Revis	42·9	22·8	6·9	,,
Ravison	90·96	34·87	27·85	10·50	,, ,,				
Locust bean meal	87·95	5·04	71·12	3·01	Smetham				

For the German method of calculating rations, in which differentiation amongst the nitrogenous substances is made, the reader is referred to The Scientific Feeding of Animals, by Kellner (English translation), 1909.

		Digestible nutrients.		
Ration as above	Dry matter. 26·4	Protein. 1·98	Carbohydrates. 11·9	Oil. 0·27
3 lb. of linseed cake	2·7	0·60	0·9	0·27
	29·1	2·58	12·8	0·54

This compares quite closely with the standard ration, and gives a nutritive value of 1 : 5·4 as compared with 1 : 5·7 as required by the standard ration. This ration would therefore form a satisfactory basis for working purposes.

The tables on pp. 325–6 gives the analytical figures and the digestibility co-efficients of a few well-known feeding stuffs. The analytical figures are a selection from a very great number published by Smetham (abstract, Analyst, xxxv, 1910, p. 54). The digestibility co-efficients applicable to them are taken from those published by Henry (Feeds and Feeding, 1898, p. 625).

Molasses   Cake.

Some feeding stuffs are made by mixing molasses with various oil-cakes and maize in particular, or are a simple admixture of the saccharine material with peat moss. The sugars may be extracted by maceration with water and estimated in the usual manner by the polarimetric or Fehling's method ($q. v$).

The following table gives the variation in composition of molasses as given by Babington (Canadian Inland Revenue Dept., Bull. xxv).

Polarisation (direct)	.	30 to	50° V
,, (invert.)	.	-10 ,,	-24° V.
Sucrose by Clerget	.	32 ,,	52 per cent.
Reducing sugar	.	13 ,,	24 ,,
Moisture .	.	29 ,,	32 ,,
Ash .	.	0·5 ,,	4·0 ,,

These figures will enable an approximate idea of the content of cane-sugar molasses present to be obtained.

A number of other analyses of feeding cakes will be
found in Chapter V under their respective oils and fats,
in the preparation of which they form a bye-product.

Analysis of Feeding Stuffs.

As feeding stuffs which are sold under " The Ferti-
lizers and Feeding Stuffs Act" have to conform to
certain regulations, the methods laid down under the Act,
as well as those which are generally sufficient and
applicable, are given.   The official determinations apply
only to the determinations of oil, moisture and albumin-
oids, and prescribe certain limits of errors of sampling,
and within these limits the composition, as stated in the
invoice, must lie.   The limits of error for oil and
albuminoids are given in Schedule II of the Fertilisers
and Feeding Stuffs (Limits of Error) Regulations, 1906,
as follows :

Feeding stuff.	Limits of error.
Cake or meal :	
Decorticated cotton	
Undecorticated cotton	
Earth nut or ground nut	
Palm kernel or palm nut .	One tenth of the percentage
Coconut .	of oil and one tenth of the
Niger seed	percentage of albuminoids
Sesamé seed.	stated in the invoice.
Sunflower seed .	
Hemp seed .	
Kurdee or safflower .	
Compound . . .	
Linseed .	One eighth of the percent-age of oil and one eighth of the percentage of albu-minoids stated in the invoice.
Rape . .	
Maize	
All other feeding stuffs, not otherwise specified in this schedule . .	One fifth of the percentage of oil and one fifth of the percentage of albuminoids stated in the invoice.

Method of Sampling (Official).

(*a*) If the sample be already in a fine condition, *e. g.* a meal, it should be thoroughly mixed and a portion for the estimation of the moisture taken at once.

(*b*) If the sample be not in a fine condition, *e. g.* a cake, it should be carefully pulverised until the whole passes through a sieve with perforations 2 to 3 mm. in diameter. It should then be thoroughly mixed, and a portion for the determination of moisture taken at once. [The authors find that, for practical purposes, the simplest method is to pass the roughly broken cake through an ordinary coffee mill (care being taken that the mill is not driven so fast as to heat the material), the residue inside the mill being brushed out and mixed with the ground sample.]

(*c*) From the sample thus prepared a portion not less than 100 grm. in weight shall be taken and further powdered, if necessary, and passed through a sieve with perforations of about 1 mm. diameter [which is quite unnecessary if a coffee-mill has been used].

(*d*) If the original sample be appreciably damp, or if the operations of pulverisation and mixing be likely to result in loss or gain of moisture, the moisture shall be determined in this portion as well as in the sample prepared as in paragraph (*b*) in order that the results of the analysis may be corrected to correspond with the sample in its original condition as regards moisture.

(*e*) Materials which cannot be conveniently pulverised or passed through a sieve should be thoroughly mixed and sampled by the most convenient means.

(*f*) The prepared portion of the sample shall be placed in a stoppered bottle, and from it the portions for analysis shall be weighed.

Moisture (Official).

A weighed quantity of the sample shall be dried at
100° C. ⟦The authors employ for this purpose large flat
stoppered weighing bottles, $2\frac{1}{4}$ inches in diameter by
$1\frac{1}{4}$ inches high, into which are weighed 3 to 5 grm. of
the material according to its bulk.⟧

Fat or Oil (Official).

A weighed quantity of the sample shall be placed in
a Soxhlet thimble, which shall then be placed in the
Soxhlet extraction tube and extracted with washed
re-distilled ether.   At the end of three to four hours
the thimble shall be removed from the Soxhlet tube,
dried, and its contents finely ground in a small mortar
previously rinsed with ether.   The substance shall
then be returned to the thimble, the mortar being
washed out with ether, and extraction continued for
another hour.

After evaporation of the solvent the oil shall be
dried at 100° C. and weighed.   The oil shall be re-
dissolved in ether, and any undissolved matter shall be
weighed and deducted.   In the case of samples con-
taining saccharine matter, such as sugar meals, the
weighed portion in the Soxhlet thimble is to be washed
twice with water and then dried previous to extraction.

⟦The method given on pp. 9–11 will be found to give
identical results in a very much shorter time, and since
petroleum ether is used, no correction of the extracted
fat is necessary.⟧

Total Protein (Albuminoids) (Official).

The percentage of albuminoids shall be ascertained
by multiplying the percentage of nitrogen by 6·25.

The determination of the nitrogen is carried out officially as follows :

A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask, 10 grm. of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless or of a light straw colour, is obtained. A small crystal of copper sulphate or a globule of mercury may be added to the liquid in the digestion flask. The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and where mercury has been used, with the addition also of sodium or potassium sulphide solution. The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, 1 grm. of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in the control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.

The following is an exact description of the Kjeldahl-Gunning method as carried out by the authors :

One grm. of the substance which has been sampled in the manner described above is weighed into a 500 c.c. Jena flask. In the case of fine meals and flours this is conveniently done in a small thin glass test-tube, one inch long and half an inch in diameter, the whole tube being dropped into the flask. Twenty-five c.c. of pure concentrated nitrogen-free sulphuric acid are added, taking care that the contents of the tube have been well shaken out before adding the acid. A small crystal of copper sulphate (about 0·2 grm.) is introduced, and the flask heated, in an almost horizontal position, over

a very small flame until all spirting has ceased, when the flame is increased until the acid is seen to be slightly
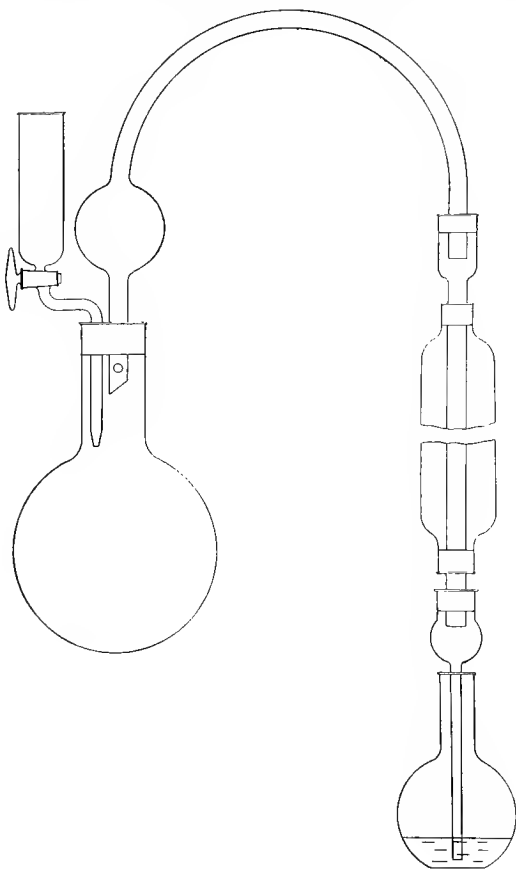
Fɪɢ. 34.

distilling above the black mass. The flame is turned out, and after the mixture has slightly cooled, 10 grm. of pure, finely powdered potassium sulphate are added

and the heating continued, the flask being now placed on a guard-disc of asbestos board, in which a hole has been cut of sufficient size to prevent the flame from touching the sides of the flask above the liquid. The heating is now pushed as vigorously as possible, until the liquid has become quite clear, any black particles on the sides of the flask being washed down by carefully swinging the contents of the flask, the heating being continued until the contents are a clear bright blue. *The heating is then further continued from this point for thirty minutes,* as conversion into ammonia is not always complete under this time. The contents of the flask are allowed to cool, 150 c.c. of water added, and the flask fitted with a double bored cork carrying a tap funnel and still head as shown in the illustration. The still head is then connected to a condenser, fitted with a bulb adapter, dipping into a flask in which have been placed 50 c.c. of N/10 sulphuric acid. A knife-point full of zinc dust is dropped into the tap funnel which is immediately filled with the necessary quantity of caustic soda solution, this being then allowed to run slowly into the flask, carrying with it the zinc dust. It is well to note that bubbling should commence in the standard acid *immediately* the alkali enters the flask, thus indicating that all connections are air-tight. The contents of the flask are brought rapidly to the boil, care being exercised that frothing does not take place as ebullition commences. The distillation is carried out as rapidly as possible and in general all ammonia will have distilled over in fifteen minutes. The adapter is then removed and a drop of the liquid falling from the condenser tested for freedom from ammonia with litmus paper. When free, the tap of the funnel is opened, and the gas turned out. The adapter is rinsed, inside and out, with a little water, and the dis-

tillate titrated with $N/10$ alkali, using methyl-orange
or cochineal as indicator.

A blank experiment is carried out in a similar
manner, using 1 grm. of pure sugar in place of the
sample. From the result so obtained the nitrogen is
calculated as follows :

The number of c.c. of alkali used plus those required
for the blank are subtracted from the 50 c.c. of the
standard acid used. The remainder, multiplied by 14
and by a factor of conversion of nitrogen into albu-
minoids, gives the percentage of albuminoids in the
sample if exactly 1 grm. has been taken.

The following points should be noted : The con-
denser should have a Jena glass inner tube. A globule
of mercury may be used instead of the copper sulphate,
in which case, after the acid digestion is finished, about
50 c.c. of water should be added and then 1 grm. of
sodium hypophosphite, the solution being warmed (if
necessary) to between $60°$ and $70°$ C., when all mer-
cury will be deposited. After this 100 c.c. more water
are added followed by the alkali and zinc dust as above
described. If methyl orange solution be used it should
first be tested for sensitiveness, as a distinct colour
change must be observed when one drop of $N/10$ acid
is added to 100 c.c. of distilled water containing two
or three drops of the indicator. For many reasons
cochineal is preferable, particularly as titrations may be
carried out by gas-light.

The alkali solution used for liberating the ammonia is
made by dissolving 3 lb. of ground caustic soda in sufficient
water to fill a Winchester quart bottle. It is useless
to attempt to filter this solution, but if it be left to
stand for a week or so, it may be syphoned off easily
into a bottle fitted with a syphon and guard tube, and
may be drawn off as required. The quantity necessary

for each experiment is ascertained by placing 5 c.c. of
the digestion acid in a beaker and running in the
alkali until neutralised. This amount multiplied by 5
will be the amount necessary to liberate the ammonia
for distillation.

Factors for Conversion of Nitrogen to Protein.

Ordinary feeding stuffs . . .	6·25
Casein	6·39
Cereals	6·25

STARCH.

(a) *Polarimetric Method* (Ewers).

This is always determined on the fat-free-dry sample.
If ready-formed sugars be not present no further pre-
paration of the substance will be necessary. If sugar
be present, stir 5 grm. in a beaker with 50 c.c. of cold
water for one hour. Pour on to a filter and wash with
250 c.c. of water. The filter is then pierced and the
contents washed into a 100 c.c. flask with hydrochloric
acid (containing 1·124 per cent. by weight of HCl) con-
tained in a wash bottle fitted with a fine jet. When
50 c.c. of the acid have been used the flask is placed in
boiling water for fifteen minutes, during the first three
of which the contents of the flask are gently rotated.
About 40 c.c. of water are then added and the contents
cooled to 20° C., when 10 c.c. of a 4 per cent. solution
of phosphotungstic acid are run on to the surface
without mixing, and the flask filled to the mark.
After mixing, the contents are filtered clear and
polarised.

The mean specific rotation of starch is taken by Ewers as—

$$[a]\,_D^{20} = 181\cdot5,$$

but if the Ventzke scale be used and a 200 mm. tube the reading obtained is multiplied by 1·912, when the percentage of starch is obtained without further calculation, if 5 grm. of material are employed.

Ewers gives the following specific rotations for various starches :

Wheat	.	.	182·7	Rye	.	.	181·0
Barley	.	.	181·5	Oats	.	.	181·3
Rice	.	.	185·9	Maize	.	.	184·5
		Potato	.	.	195·4		

When no sugar is present the meal may introduced directly into the flask, in which case it is well shaken in the flask with 25 c.c. of the acid, and the sides are then washed down with a further 25 c.c. before heating in the water bath.

(b) Starch by Diastase.

About 5 grm. of the fat-free-dry material are washed on a filter with 150 c.c. of 10 per cent. alcohol and then with 10 c.c. of 95 per cent. alcohol. The residue on the filter is washed into a 250 c.c. graduated flask with about 50 c.c. of water, and the flask immersed in boiling water with constant shaking for at least fifteen minutes. It is then cooled to 55° C. and 0·1 grm. of diastase (mixed with a little water) added, and the mixture maintained at 55°C. for an hour. It is then rapidly heated to boiling, again cooled to 55° C., and the diastase treatment repeated for one hour. The mixture is then cooled, made up to the mark and filtered; 200 c.c. of the filtrate are mixed with 20 c.c. of hydrochloric acid (sp. gr. 1·125) and

heated in boiling water under a reflux condenser for two and a half hours. The mixture is then cooled and sodium hydroxide solution added until the reaction is only faintly acid, and the volume then made up to 500 c.c. The dextrose is determined volumetrically by Fehling's method (p. 314 *et seq.*). The amount of dextrose found,
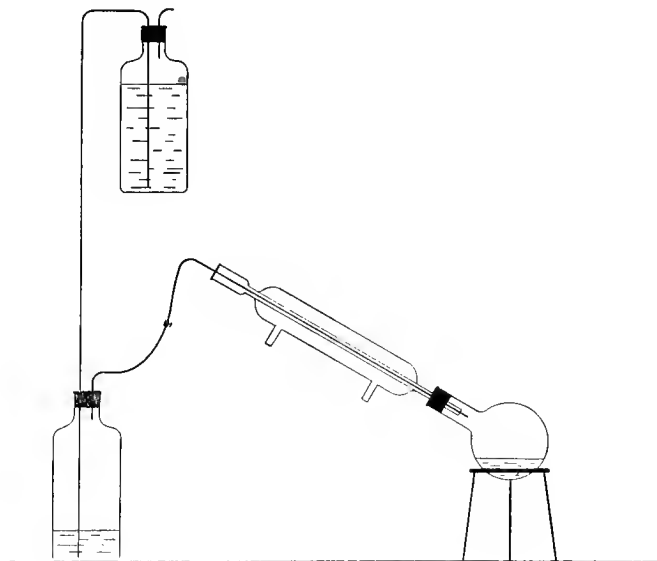
FIG. 35.

multiplied by 0·9, will give the amount of starch, which is then calculated on the 5 grm. taken.

CRUDE FIBRE.

One grm. of the fat-free-dry material is weighed into a 300 c.c. flask and 100 c.c. of boiling 1·25 per cent. sulphuric acid added. The flask is connected to a reflux condenser and brought rapidly to the boil,

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and the boiling continued for thirty minutes exactly. The contents of the flask are then rapidly filtered on a pump plate covered with a piece of fine well-washed linen cut one eighth of an inch larger than the diameter of the plate, the pump being in full operation before any liquid is poured on to the linen. The flask is rapidly washed out with boiling water, which is poured over the material on the plate (about 100 c.c. of water usually suffices). The funnel is then placed in the mouth of the digestion flask, the linen lifted with forceps, the plate removed and the residue washed back into the flask with 100 c.c. of boiling 1·25 per cent. sodium hydroxide solution contained in a wash bottle. The flask is then again connected to the reflux condenser and the contents boiled for thirty minutes exactly.

The contents are then filtered on a plate as before, using a circular tared filter-paper instead of the linen (the best quality ashless filter-paper must be used for this purpose). The whole of the contents of the flask are washed on to the filter with boiling water, and the washing continued until the residue is free from alkali. Ten c.c. of 10 per cent. acetic acid are then poured over the residue on the filter, which is washed once or twice more with hot water, and then once with hot, strong, alcohol. The filter is carefully lifted off the plate, placed in its weighing bottle, any particles on the sides of the funnel being carefully removed and added to it, and the whole dried to constant weight. The filter is then ashed, and the weight of the residue less this ash is calculated in percentages on the original sample and is returned as " crude fibre." In order to prevent frothing, a gentle stream of air should be introduced through a small tube placed down the centre of the condenser to just inside the neck of the flask. A simple method of effecting this is shown in Fig. 35.

The acid and alkali used in the above method must be accurately standardised by titration, and the alkali should be free from carbonate.

Ash.

Two to three grm. of the material are burnt in a platinum dish at the lowest possible temperature. Where difficulty is experienced in obtaining a white ash (as, for example, in the case of maize germ cake), it is better to just char the substance, and to extract the char with water, which is poured through a small filter. The filter is then placed in the dish and the whole burnt to a white ash. The water extract is then added, evaporated to dryness on the water bath, and the whole again gently ignited.

After weighing the *total ash*, it is dissolved, as far as possible, in hot dilute hydrochloric acid. The insoluble residue is filtered off, ignited and weighed. This is returned as *sand*, but it will be understood that this is not the total silica, which, if required, may be estimated in the acid filtrate from the sand in the usual manner.

The following determinations are less often required than the foregoing :

Albuminoid Nitrogen (Soluble).

(American official method.) Place 0·7 grm. of the substance in a beaker, add 100 c.c. of water, and heat to boiling (or if the substance be rich in starch heat on the water bath for ten minutes), and add so much of Stutzer's reagent as shall contain 0·5 grm. of cupric hydroxide ; stir thoroughly, allow to cool, and when cold, filter, wash the residue on the filter well with cold water,

and estimate the nitrogen by dropping the filter and contents into a flask, proceeding as described above under " Total Protein," it not being necessary in this case to add any copper. When examining oil-cake or other substances rich in alkaline phosphates, it will be necessary to add 1 or 2 c.c. of a concentrated solution of potash alum (free from ammonia) immediately before the addition of the cupric hydroxide.

Stutzer's reagent is prepared as follows :

100 grm. of pure $CuSO_4$ are dissolved in 5 litres of water, adding 2·5 c.c. of glycerol. A dilute solution of sodium hydroxide is then run in until the liquid is alkaline, the precipitate is allowed to settle, the supernatant liquid poured off and the precipitate rubbed up with water containing 5 c.c. of glycerol per litre and washed by decantation until free from alkali. The precipitate so obtained is rubbed up with water containing 10 per cent of glycerol into a thin gelatinous mass which can be just measured with a pipette. The cupric hydroxide per c.c. of the preparation is then determined.

AMIDE NITROGEN.

A weighed quantity, about 1 grm., is boiled with 100 c.c. of 5 per cent. hydrochloric acid for thirty minutes under a reflux condenser. The solution is then just neutralised to methyl orange with a solution of sodium carbonate, and, after the addition of an excess of magnesium oxide, distilled into standard acid in the ordinary way. The ammonia so obtained is usually calculated as *asparagin* $C_2H_3 (NH_2) (CONH_2) COOH$, and returned as *amido compounds*.

1 molecule $NH_3 = 1$ molecule of asparagin.

Phosphoric Acid and Potash.

10 grm. of the fat-free-dry substance are weighed into a 500 c.c. Jena flask and a mixture of 30 c.c. of concentrated nitric acid and 5 c.c. of concentrated hydrochloric acid added. (If the mixture is not then liquid the quantity of acid must be increased.) The flask is gently heated over a small flame, which is gradually increased until a clear liquid is obtained. The solution is cooled, cautiously diluted with water and made up to 250 c.c.

In this solution phosphoric acid and potash are determined.

Phosphoric acid (Pemberton's method, A.O.A.C. modification).—25 c.c. of the acid solution (unless the percentage of phosphoric acid is expected to be more than 5, in which case not more than 10 c.c. should be used) are taken. To this are added 5 to 10 c.c. of nitric acid, and then ammonium hydroxide until nearly neutral, and the whole diluted to 70 or 80 c.c. and heated in a water-bath to $60°–65°$ C.

Twenty to 25 c.c. of freshly filtered molybdate solution are added and the mixture stirred and allowed to stand for fifteen minutes. The liquid is then rapidly poured off through a Gooch filter having as thin a layer of asbestos as will be sufficient to retain the precipitate, and the precipitate in the beaker washed twice with water (25 c.c.), stirring well and allowing to settle before pouring off the washings through the filter. The precipitate is now washed on to the Gooch with cold water and the washing continued till 20 c.c. of the washings do not decolourise the colour produced by 1 c.c. of the standard sodium hydroxide solution with phenolphthalein. The asbestos wad and the precipitate are carefully picked out and dropped into a flask, the

Gooch placed in a small funnel in the mouth of the flask and washed with 10 c.c. of the standard sodium hydroxide solution to remove any particles of the precipitate left in the Gooch. The Gooch and funnel are then thoroughly washed into the flask with water, the flask closed with an india-rubber stopper, and the contents shaken with a rotary motion until the asbestos is thoroughly broken up. The standard alkali is then added until the yellow precipitate is completely dissolved, about 5 c.c. being then added in excess of the necessary quantity. The contents of the flask are thoroughly mixed, and after the addition of a few drops of phenolphthalein, titrated back with the standard acid. The total number of c.c. of standard sodium hydroxide used to dissolve the precipitate, less the number of c.c. of standard acid required to titrate back $\times 0.001 =$ grm. of P_2O_5 in the number of c.c. of the original solution used.

The reagents required are made as follows :

Molybdate solution.—100 grm. of molybdic acid dissolved in a mixture of 144 c.c. of ammonium hydroxide (sp. gr. 0·90) and 271 c.c. of water, are added slowly and with constant stirring to a mixture of 489 c.c. of nitric acid (sp. gr. 1·42) and 1148 c.c. of water. The mixture is kept in a warm place for several days and decanted for use. For the above method 100 c.c. of this solution are mixed with 5 c.c. of nitric acid (sp. gr. 1·42) and filtered just before use.

Standard sodium hydroxide solution.—Dilute 323·8 c.c. of N/NaOH solution to 1000 c.c. 1 c.c. of this solution $= 0.001$ grm. of P_2O_5.

In order to avoid the presence of carbonate in the standard sodium hydroxide solution, it is advisable to place about twice the required weight of solid caustic soda in a separator and to add just sufficient water to

wash the surface of the sticks. This water is rapidly run off and the process repeated. By this means the carbonate, which is on the outside, is washed away. Sufficient water is then added to dissolve the residue in the separator, and after solution has been effected the liquid is run out into a graduated flask, made up to a definite bulk, and its strength ascertained by titration against standard acid. It can then be adjusted by dilution to the required strength.

Standard acid solution.—This solution is made exactly equivalent to the above alkali solution, using phenolphthalein. The acid is to be run into the alkali in setting the solution. Any mineral acid may be used.

Potash.

100 c.c. of the solution of the substance, made as directed under phosphoric acid, are evaporated to dryness, taken up with a little water and hydrochloric acid, and again evaporated to dryness, any silica which separates being filtered off, and washed till free from chlorides. The combined filtrate and washings are made alkaline with pure sodium carbonate, and boiled till free from ammonia. The solution is washed into a beaker and made up to 250 c.c. approximately with water, 20 c.c. of hydrochloric acid cautiously added and the whole brought to the boil. A solution of barium chloride (containing 127 grm. $BaCl_2.2H_2O$ and 125 c.c. of pure concentrated hydrochloric acid per litre) is dropped in with constant stirring until *all* sulphates are precipitated. The solution is boiled for a few minutes, cooled, filtered and evaporated to dryness. The residue is taken up with 20 c.c. of hot water and sufficient perchloric acid added to combine with one and a half times the bases present (5 c.c. of acid sp.

gr. 1·5 will probably be sufficient). The mixture is evaporated with stirring to a syrupy consistency, dissolved in a little hot water, 5 c.c. of perchloric acid added and evaporated till white fumes of the acid are given off strongly, again diluted, and 2 c.c. of perchloric acid added and again evaporated. The residue while still warm, is well stirred with 20 c.c. of acid alcohol (97 per cent. alcohol, containing 0·2 per cent. of perchloric acid). The undissolved portion is allowed to settle, and the liquid decanted through a tared Gooch crucible with an asbestos pad, the residue in the dish being warmed with another 20 c.c. of acid alcohol, thoroughly disintegrated, and the liquid again decanted, this treatment being once more repeated. The residue in the dish is then dissolved in 10 c.c. of hot water, a little perchloric acid added, and the whole again evaporated until it fumes strongly. The residue is mixed with 5 c.c. of the acid alcohol and the mass transferred to the Gooch crucible with further quantities of acid alcohol. (Not more than 50 c.c. of the acid alcohol should be required for all the above washings.) The Gooch crucible is then rinsed with 1 or 2 c.c. of 97 per cent. alcohol and dried at 130° C. to constant weight. Weight of $KClO_4 \times 0·3402 = K_2O$ in the original 100 c.c. used. In using the above process, which is really much more rapid than the description would imply, great care should be exercised in thoroughly disintegrating the mass of perchlorates with the acid alcohol, in order that those other than potassium perchlorate should be properly dissolved out. The process is quite as accurate as the platinum method, and pure perchloric acid is prepared by Kahlbaum at a price which brings this process much below the cost of the platinum method. The above method presupposes the use of perchloric acid of sp. gr. 1·5 to 1·6. The acid is perfectly safe and non-explosive.

CHAPTER IX.

MILK.

It is not intended in this chapter to enter into the full details of the analysis of milk and cream, etc., but to give such methods and tests as will probably be useful to the margarine manufacturer in controlling the milk employed by him.

The control of milk will include an ordinary analysis for chemical composition, and for the presence of preservatives which would be deleterious to the subsequent "souring," tests for any previous pasteurisation, and also for the control of pasteurisation employed in actual manufacture, and some simple methods of judging the bacteriological condition of the milk supplied, in order to avoid as far as possible the development of "taints" in the soured milk or in the margarine itself.

ANALYSIS OF MILK.

Total Solids.

2·5 grm. of the samples are weighed out into glazed porcelain dishes about $2\frac{3}{4}$ in. in diameter, flat-bottomed, and about $\frac{1}{2}-\frac{3}{4}$ in. in depth. One c.c. of acetone is added to each, and the dishes placed on a rapidly

boiling water bath for thirty minutes, and then placed in the bath for forty-five to sixty minutes longer, the outsides being first carefully wiped with a towel. They are then weighed in the following manner :

To avoid the use of a desiccator, the dishes are placed in the oven in order of ascending weights. The first is taken out and placed on a wire tray beside the balance. While still gently warm the dish is placed on the balance and rapidly counterpoised. It is then replaced on the wire tray and the second dish removed from the oven. The rider is now shifted up 1–2 mgrm., and immediately the first dish is just cool (as ascertained by touching against the cheek) it is replaced on the balance, and the needle allowed to swing. If the divisions on the scale corresponding to a difference of 1 mgrm. are known (2 is a suitable number in order to get rapid swings) the weight is easily ascertained to the nearest milligramme without further alteration of the rider. By this time the second dish will be sufficiently cool to deal with, and so on. The weights of the dishes themselves, when empty, are ascertained in an exactly similar manner, and need re-determining every three to four weeks. Using 2·5 grm. the actual weight of milk solids multiplied by 40 gives the percentage of total solids in the sample.

Fat.

For routine purposes the Gerber method is the simplest and quickest. The necessary butyrometers and centrifuge may now be obtained anywhere, and the chemicals employed are simple and as easily procured.

Reagents.—Sulphuric acid (commercial) . Sp. gr. 1·820–1·825. Acids of a higher gravity may be diluted, but the gravity must not be less than 1·820.

Amyl alcohol.—The fraction boiling between 124° and 130° C. and having a specific gravity of 0·815–0·818 is employed. It should be practically colourless.

Making the test.—Ten c.c. of the acid are placed in the butyrometer and 11 c.c. of the sample run in on to the acid down the side of the butyrometer, so that the acid and milk do not mix. One c.c. of the alcohol are run in on to the milk, and the mouth of the butyrometer closed by screwing in a tight-fitting india-rubber stopper. The tube is then violently shaken up and down in the direction of its length till all the milk is dissolved, and then placed in a bath of water at 160° F. for five to ten minutes (not more than twenty). It is then placed in the centrifuge and whirled for five minutes at about 2000 revolutions per minute. The fat, which has collected in the graduated neck, is read off, the readings being in direct percentages of fat, the larger divisions being units. The fat layer should be quite clear, and there should be no plug of undissolved material below it, which latter indicates insufficient shaking and heating. It is advisable to make a blank experiment with the acid and alcohol, using water instead of milk, in order to see that no insoluble matter is obtained from them.

It is also very advantageous to check the readings of the tubes against some standard method of fat analysis. Such a method is the—

Gottlieb Process.

For this the following reagents are required :

(1) Strong alcohol (95 per cent. by volume).

(2) A solution of ammonia (made by mixing 100 c.c. of 0·880 ammonia with 100 c.c. of water).

(3) Methylated ether, sp. gr. 0·720.

(4) Petroleum ether, distilling below $40°$ C., and leaving no residue.

Apparatus.—A strong glass tube about $\frac{3}{4}$ in. in diameter and holding 50 c.c. fitted with an indiarubber
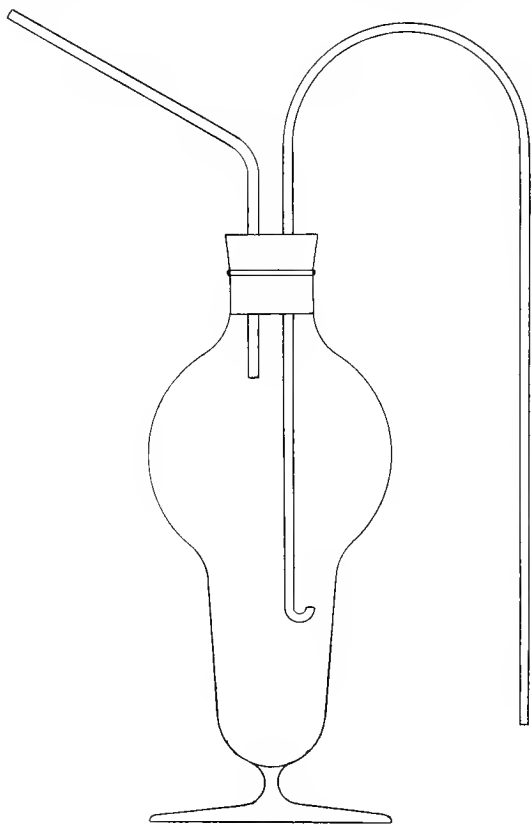
Fig. 36.

stopper. Instead of this tube, the apparatus shown in Fig. 36 will be found of great advantage (Eichloff and Grimmer).

In the tube or apparatus are placed 5 grm. of milk, 0·5 c.c. of ammonia solution added, and the contents mixed by swinging the tube in a circular manner. Then 5 c.c. of alcohol are added, the whole again mixed, 12·5 c.c. of methylated ether run in and the stopper inserted. The tube is inverted three times, after which 12·5 c.c. of petroleum ether are run in and the tube again inverted three times (any violent shaking must be avoided). The tube is allowed to stand and settle out ; the ether solution is then blown off into a weighed flask, by means of a wash bottle arrangement (shown in place in Fig. 36), down to $\frac{1}{4}$ in. from the aqueous layer. A fresh quantity of petroleum ether (or mixed ethers recovered from other tests) is run into the tube, and the contents mixed once by inversion. This ether is then blown off and the process repeated once more. The ether is then distilled off from the fat and the flask dried to constant weight in the water oven.

Acidity.

The method of estimating the acidity in milk commonly employed in this country consists in adding N/10 NaOH to the milk until a faint pink colour is given in the presence of phenolphthalein. The test, in the case of milk, is carried out conveniently as follows :

Twenty c.c. of the milk are placed in each of two test-tubes (6 in. by 1 in.), and to one of these about five or six drops of 1 per cent. phenolphthalein solution in 50 per cent. alcohol are added, and then N/10 NaOH, about four drops at a time, until, after gently shaking, a very faint pink colour is noted in the milk as compared with the colour of the control. Then "the number of c.c. of N/10 alkali required to produce this result multiplied by 5 gives the so-called *degrees* of acidity."

Good fresh milk from normal cows in good condition usually has an acidity of 15 to 18, which will not increase perceptibly during the next twenty-four hours if the milk has been cooled immediately after milking and subsequently kept at a reasonably low temperature. Milk with 20 to 22 degrees of acidity has a slight sour taste, quite perceptible to the educated palate. When 24 degrees is reached the milk usually coagulates on boiling. When estimating the acidity in milk which has been soured for the purposes of churning, it is preferable to measure out the required quantity into a porcelain dish or a cup, and to carry out the titration in this, rather than as described above, the acidity in such cases being much higher than is the case with fresh milk. In the case of milk soured for churning, it is more usual to express the acidity in *percentages of lactic acid*, taking 1 c.c. of N/10 alkali to equal 0·009 grm. of lactic acid. For simplicity in this case 9 grm. of milk are pipetted into the dish (from a special pipette) when

$$\frac{\text{c.c. of N/10 alkali}}{10} = \text{percentage of lactic acid.}$$

The following very useful method of titrating the acidity of milk has been devised by Richmond (Analyst, 1912, vol. xxxvii, p. 168), and enables acidities to be determined correctly by artificial light, and obviates any difficulties arising from the colour-blindness of the operator, as only shades of colour are compared and not the colours themselves. It is carried out as follows :

To the milk in the control tube is added one drop of a 0·01 per cent. solution of rosaniline acetate in 96 per cent. alcohol, and to the other tube 1 c.c. of 0·5 per cent. phenolphthalein solution. The alkali is run into the latter until the depth of colour in it, on shaking, is

identical with that of the control. The figure so obtained is about 1·5 degrees higher than by the usual method, and should be distinguished as "*Acidity by the Rosaniline (R.S.) Standard.*"

Preservatives.

Boron compounds.—About 1 c.c. of the milk are placed in a flat dish similar to that employed for total solids, and thoroughly mixed with one drop of strong hydrochloric acid and then with five to six drops of saturated alcoholic solution of turmeric. The dish is then placed on a rapidly boiling water bath, and the mixture evaporated to dryness. In the presence of as little as 0·02 per cent. of boric acid the edge of the residue will assume a *salmon-pink* colour immediately it is dry, while, if no boron compounds be present, the residue will be a *dirty yellow*.

Formalin.—The presence of formalin or its compounds will be detected during the fat estimation by the Gerber process. In the presence of formalin the junction of the milk and acid before shaking will assume a violet colour, pure milk giving only a brownish-yellow tinge. It is to be noted that excessive quantities of formalin do not give the purple colour, but in such cases, apart from the taste of the milk, its presence would be suspected on account of the great difficulty with which the curd dissolves in the Gerber tube when shaken.

Salicylic and benzoic acids.—Not less than 100 c.c. of the milk are heated in boiling water after the addition of 4 c.c. of 10 per cent. sodium carbonate solution per 100 c.c. of milk used. When the mixture has attained the temperature of the water, a volume of 20 per cent. calcium chloride solution equal to that of

the sodium carbonate solution employed is run in, when precipitation of the casein should occur.

The contents of the flask are rapidly cooled and filtered, and the test finished exactly as described on p. 111 for the alkaline extract of butter or margarine.

Pasteurisation.

It will often be necessary to ascertain whether the supply of milk has been pasteurised previous to delivery, and in any case it will be of importance to control the efficiency of the pasteurising process employed in the factory. Two forms of pasteurisation are commonly employed :

(1) That in which the milk passes continuously through a steam-jacketed vessel, being caused to pass over the heated surface in a thin film by means of a paddle, the milk then passing out on to a cooler. This method is usually termed "flash" pasteurisation.

(2) That in which the milk is run into a jacketed vessel, and, while being steadily stirred, brought to the necessary temperature by carefully admitting steam to the jacket, and subsequently held in the pasteuriser at the required temperature with constant stirring for the necessary time. In the opinion of the authors the second method is greatly superior in every way to the former for milk which is to be used for souring, as not only can the necessary temperature be maintained throughout the bulk of the milk, but a much lower temperature can be efficiently employed, with great gain in the flavour of the product. The efficiency of the operation also can be much better controlled by chemical tests.

Of the methods which have been suggested for the detection or control of pasteurisation (and they are

legion), the two following are recommended as being
the most practical and efficient :

(1) *Benzidene acetate test.*—This test, which can be
rapidly carried out, is satisfactory for determining
whether the milk has been heated to a certain tem-
perature for a definite time, but while quicker, is not
so sensitive as the next method described. It is
carried out in the following manner, and in compara-
tive work it is necessary to adhere to the quantities
given :

Five c.c. of the milk are placed in a test-tube,
1 c.c. of a 4 per cent. alcoholic solution of benzidene
added, and the whole shaken ; one drop of pure acetic
acid is then added and the whole again shaken. Three
c.c. of hydrogen peroxide solution (20 volumes) are then
allowed to run carefully on to the surface of the
mixture in the test-tube. The following results are
obtained :

Sample.	Temperature of pasteurisation.	Time of pasteurisation.	Result.
(1) Unheated	. .	. .	Deep azure blue.
(2) Pasteurised	151° F. .	Up to 45 min.	Slightly less than (1).
(3) ,,	158 to 160° F.	30 min.	As (2).
(4) ,,	,,	45 min. .	Faint blue.
(5) ,,	162 to 163° F.	. 15 min.	Very faint blue.
(6) ,,	,,	30 min.	Colourless.
(7) ,,	176° F.	1 to 2 min. .	Colourless.

The benzidene solution keeps indefinitely in the
dark.

(2) *Para-phenylenediamine-guaiacol test* (Hesse and
Kooper).—This test, though not so rapid of application
as the former, permits (in the following slightly modi-
fied form of the original test) of very exact estimations
of the degree of pasteurisation.

Reagents.—(1) Para-phenylenediamine hydrochloride
2 grm. dissolved in 75 c.c. of 95 per cent. alcohol.

(2) Guaiacol (crystallised) 1 grm. dissolved in 15 c.c.
of water and mixed with 60 c.c. of alcohol.

23

Fatty Foods

Equal volumes of these solutions are mixed for use.

Method of carrying out the test.—Forty c.c. of the milk are mixed with 6 c.c. of basic lead acetate solution (see p. 310), well shaken and allowed to stand for five minutes. The mixture is then filtered and 5 c.c. are placed in a 50 c.c. Nessler glass, and one drop of 20 volume hydrogen peroxide and two drops of the mixed reagent added. After allowing to stand five minutes water is added to the 50 c.c. mark and the whole filtered (if necessary).

Working in this way the colour given by the test of the pasteurised milk is readily matched against such a volume of the test of the original milk as will give the same colour.

The following table has been compiled by the authors. The number of c.c. given in the various columns are the number of c.c. of the test of the original unpasteurised milk, which gave the same depth of colour as the full 50 c.c. obtained from the pasteurised milk. All the pasteurisation tests were carried out by holding the milk in bulk at the temperature named in an experimental pasteuriser. It must be clearly understood that the figures, though probably strictly comparable among themselves, may not be absolutely correct for all actual conditions. A few tests carried out on the actual plant will show what corrections it will be necessary to apply.

Temperature of pasteurisation.	Duration of pasteurisation.		
	15 min.	30 min.	45 min.
151° F.	45 c.c.	41 c.c.	44 c.c.
156° to 157° F.	39 ,,	40 ,,	35 ,,
158° to 160° F.	21 ,,	12 ,,	7 ,,
162° to 163° F.	4·5 c.c.	0 ,,	0 ,,

In the above experiments, samples which were withdrawn from the pasteuriser after the specified time, were cooled at once, and the further destruction of the enzymes prevented, which would not be the case in

practice. In actual practice the time which elapses while the pasteuriser is emptying on to the cooler must be taken into account.

The progressive destruction of enzymes as the temperature rises is well illustrated by the following figures :

Milk was steadily heated until it had reached 150° F., when samples were withdrawn as various higher temperatures were attained, the times being noted at which these temperatures were reached, starting from the time at which the milk reached 150° F.

Temperature.	Minutes elapsed after 150° was reached.	Degree of pasteursation.		
161° F.	5	(39½ c.c.)	21	per cent.
163° F.	9	(33½ c.c.)	33	,,
167° F.	15	(20 c.c.)	60	,,
167° F.	maintained for fifteen minutes	(0 c.c.)	100	,,

As the maintenance of a temperature of 165° F. for twenty to thirty minutes is amply sufficient for pasteurisation, it will be seen from the above figures how easily this can be controlled, and the variety of ways in which the same results can be produced, taking destruction of peroxydase and destruction of vegetative forms of bacteria as occurring simultaneously.

GENERAL TESTS FOR CLEANLINESS AND BACTERIOLOGICAL CONDITION.

For this purpose also methods have been produced in an increasing stream. By far the greater number are of very doubtful utility and are based on principles of which the fundamental characters are not yet clearly understood. The following yield information of a definite and useful character and are simple in application.

(1) *The Sediment Test.*

In all milk intended for souring there should be no appreciable amount of dirt. This is easily ascertained by placing 50 to 100 c.c. of the milk in a conical test glass, and allowing to stand for one to two hours. A glass rod carrying a small indiarubber plug is then carefully lowered into the milk so as to isolate the sediment. The remainder of the milk is poured off, and the upper part of the test glass washed out, keeping the rod in position. About 50 c.c. of water are then poured in, and the sediment well mixed with the water by stirring with a rod. After an hour's standing the supernatant water is poured away, the sediment drawn up with a fine capillary tube and examined microscopically under a $\frac{1}{4}$-in. objective. It is quite easy to distinguish the dirt, characteristic of uncleanly milking, which will consist largely of particles of straw mixed with, and coloured by fæcal matter, from the sandy character of the deposit which results from the conditions of transit. If, in addition to the dirt, at the first standing there is more than a trace of whitish or very slightly yellow matter, the milk should be poured off and a portion of this deposit spread upon a glass slip (3 by 1), dried by gentle warming, fixed by passing through the flame of a bunsen burner half a dozen times, stained by immersion in a 1 per cent. aqueous solution of methylene-blue for one minute, washed in water, and after dropping on some oil, examined under a $\frac{1}{12}$-in. oil-immersion lens. If the deposit is then seen to consist almost entirely of cells similar to those shown in Plate V, fig. 2, it is not improbable that there may be one or more cases of mastitis among the cows supplying the milk. Under these circumstances it may be advisable to have the cows examined by a vet-

FIG. 1.
Lactic acid-forming organisms.
× 1000.

FIG. 2.
Cellular elements in milk sediment.
× 1000.

PLATE V.

Fig. 1.
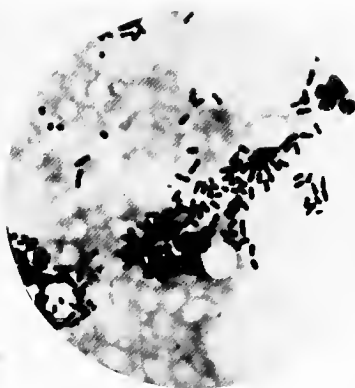
Fig. 2.
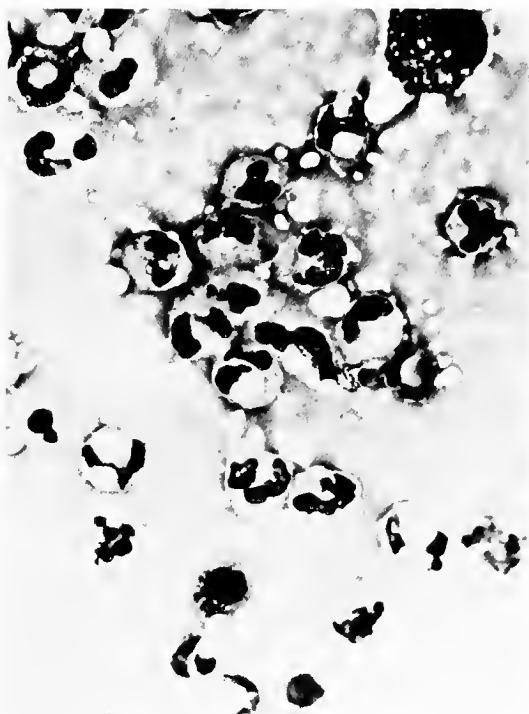
erinary surgeon. A certain number of these cells are always present in milk, and it is only when an excessive number are present that any deductions as to disease can be made, and in some cases very large numbers of these cells are found in milk from quite healthy cows. The presence, therefore, of even large numbers only justifies a veterinary inspection.

(2) *Fermentation Test.*

For the purpose of this test several large test-tubes about 6 in. by $1\frac{1}{4}$ in. and fitted with loose metal covers are required. These tubes, with the covers on, are cleaned and sterilised, either in an ordinary hot-air steriliser, or if this be not available, by thorough rinsing with boiling water.

Method of carrying out the test.—In each tube are placed 50 or 100 c.c. of the various milks to be examined, for preference as soon after arrival of the milk as is convenient. The tubes, being closed with the covers, are placed in a water bath or incubator which can be maintained at between $38°$ and $40°$ C.

After twelve hours' incubation the tubes are removed and examined. Good, fresh, well-cooled and cleanly-handled milk will as a rule not have coagulated in this time, or if it has done so, the milk will have set to a uniform gelatinous curd, free from all bubbles, and from any separation of whey between the cream layer and the milk. The curd will have no unpleasant smell, and should possess a sharp, agreeable, sour taste, leaving no unpleasant after-flavour. It is by no means uncommon, however, for a considerable contraction of the curd to take place at the sides of the tube, and consequently the appearance of whey even in the case of good milk. In such cases, however, the whey is always

very turbid and there are no gas-bubbles when the tube is gently shaken. The appearance is, however, quite distinct from that mentioned below in which digestion of the casein has taken place, under which circumstances the whey is clear and at the bottom of the tube. If the milk has not been so cleanly handled, the curd will be seen to be streaked with bubbles, and a small quantity of whey will probably be noticed between the cream and the curd. In these cases the milk has often an unpleasant smell, and the acidity may be distinctly bitter. Under worse conditions there may be considerable digestion of the casein, with separation of whey at the bottom of the tube, and the cream may be filled with bubbles of gas. Any condition other than the first one described must be considered as prejudicial to proper souring of the milk for margarine purposes. It must be clearly understood that pasteurisation is no panacea for uncleanly dairying, as not only is the souring proper prejudiced, but taints, already developed in the milk, will persist and often increase in the finished product. It may be noted that milk which has been pasteurised may produce in twenty-four to thirty-six hours a coagulum which afterwards slowly digests, and is usually alkaline (the curd being a rennet curd), or the reaction described under the next heading may take place. A small portion of the curd obtained in any case may be spread on a slide, stained, and examined as described in the last section, when it will be found that in the curd of good milk practically the only organisms present are small diplococci and short streptococci usually not exceeding four to six members, though longer chains are frequently found. This appearance is shown in Plate V, fig. 1.

When the milk has been dirtily handled the bacterial flora is usually much more diverse, and " bacil-

lary " (rod-shaped) forms are generally to be seen. The curd of pasteurised milk is usually quite free from " coccoid " forms and probably only rods will be present, generally rather large in character.

This fermentation test probably furnishes more useful information than any other, and its extreme simplicity renders it very appropriate for control purposes.

It has been considerably elaborated by some investigators and some rather fine distinctions drawn as to the results obtåined, but for these a manual dealing with milk must be consulted.

(3) *The Enteritidis Sporogenes Test.*

This test furnishes, in the opinion of the authors, considerable evidence as to the amount of cow dung which has been allowed to get into the milk, though the milk may have been subsequently cleaned by some efficient type of filtration.   The test is simple in character, requires no bacteriological apparatus, and further, as the organisms concerned in the reaction do not increase in number during transit, the findings are true for the milk as dairied.

Method of carrying out the test.—A number of test-tubes 6 by ¾ in. are plugged with cotton-wool and sterilised in a hot-air steriliser at 150° C. for three quarters of an hour, or in an oven until the cotton-wool begins to turn brown.   With a 10 c.c. pipette, which has been sterilised by rinsing out with boiling water, or by thorough heating in the flame of a bunsen burner, 10 c.c. of each milk are placed in the sterilised tubes, the cotton-wool plugs being singed before removal, and so held that the lower ends do not touch anything. About ¾ in. of melted vaseline is now poured on to the surface of the milk in each tube, the plugs being then replaced.   The tubes are now immersed in water at

80° C. and kept at this temperature for twenty minutes. They are then cooled and maintained at 38° to 40° C. for twenty-four hours.   In the case of milk which has been dirtily handled the milk will have undergone a profound change.   Very considerable digestion of the casein will have taken place, resulting in the production of whey in which the remnants of curd, torn and disintegrated with gas, float.   The vaseline plug is usually forced, by the excessive gas evolution, more or less completely up the tube, and the culture, when opened, has a distinct smell of butyric acid.   The characteristic appearance of the curd is well seen in Plate VI, fig. 1, and if some of this curd be stained and examined microscopically it will be found to contain stout bacilli with rounded ends, as seen in Fig. 2.

Milk which has been cleanly handled will either undergo no change or will set to a solid curd, which will gradually contract with the separation of whey, but without any gas-formation.

Cream and Separated Milk.

These will usually appear in margarine factories as bye-products, and practically the only examination of them that will be necessary will be an estimation of the fat.   For this purpose the Gerber method is satisfactory in both cases.

The estimation of the fat in cream.—About 1 grm. is weighed out in a small funnel, having a small rod inserted in its tube.   The cream is then washed into the ordinary Gerber bottle with two quantities of 5 c.c. of warm water.   The tube and contents are then cooled and the usual 10 c.c. of sulphuric acid and 1 c.c. of amyl alcohol added, the test being finished as in the case of milk.   If the tube be read on removal from the rotator without re-warming it will be found that:

FIG. 1.
Characteristic appearance of curd in
Enteritidis sporogenes Test.

FIG. 2.
B. enteritidis sporogenes from milk culture.
× 1000.

PLATE VI.

Fig. 1.

Fig. 2.
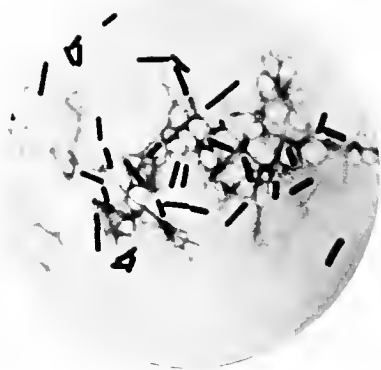
$$\text{Fat per cent.} = \frac{\text{Reading} \times \text{factor}}{\text{Weight of cream used.}}$$

The value of the factor, as determined by the authors, is as follows .

For 55 per cent. fat = 11·07

" 45 " " = 11·23

" 20 " " = 11·41

For rapid internal control a simple estimation of the total solids of the cream as suggested by Mats Weibull is quite satisfactory. The following formula is used :

$$\text{Fat per cent.} = 1 \cdot 1 \times T - 9 \cdot 5,$$

where T is the estimated total solids.

The total solids are conveniently estimated by carefully boiling off the water in a flat porcelain dish in a manner exactly similar to the method of Patrick described under butter, or by heating on the water bath as for the total solids in milk, until constant in weight.

The estimation of Fat in Separated Milk.

For the control of separators the residual fat in the separated milk may be estimated with quite sufficient accuracy in the ordinary Gerber tube. In this case, however, the tube, after rotation, is placed in water at 160° F. for two or three minutes and again rotated for five minutes, again placed in warm water and read warm—the reading being taken from the bottom of the fat layer to a point half way between the lowest point of curvature and the tip of the horns of the meniscus.

The results obtained by the Gerber process are usually lower than those obtained by the use of such a method as the Gottlieb or other extraction process, but as any fat which will not rise in the Gerber tube will in all probability not be thrown out by the separator, it is scarcely fair to judge the efficiency of separators by extraction methods.

Appendix D (*to* p. 309).

Chocolate.

Typical example of method of calculation and interpretation of the results of analysis of a sample of cheap chocolate.

Analytical data obtained.

	Percentages on dried sample.
Fat	29·00
Nitrogen	0·78 (N.)
Fibre.	1·60 (F.)
Starch (by diastase method)	6·80 (S.)
Cold water extract	52·24
Cane sugar	48·00
Cold water extract less cane sugar	4·24 (T.)
Levigation residue	2·05

Microscopical examination revealed maize starch and a fair proportion of cocoa shell.

The percentages of fat-free-dry cocoa matter (X.) and added starch (Y.) are calculated by the formulæ on page 309, substituting the above analytical figures where indicated, after allowing for cane sugar and fat as follows :

Since 100 parts of the dry sample contain 77 per cent. of fat + cane sugar, the figures for (N), (F), (S), and (T) must be multiplied by $\frac{100}{23}$ to obtain the percentage in cocoa matter + starch. The values so obtained are :

$(N = 3·39)$ $(F = 6·96)$ $(S = 29·55)$ $(T = 18·43)$.

By substitution :

$$100 \left(\frac{100\ T - CS}{2400\ - S_cC} \right) = X = 76 \text{ per cent.}$$

$$\text{and } 100 \left(\frac{24\ S - TS_c}{2400 - S_cC} \right) = Y = 22 \text{ per cent.}$$

assuming in the above an approximate value of 10 for S_c and taking the value 0·8 for C from the table on p. 308.

Employing the other formulæ, in which no assumption is made for S_c, the following values are obtained :

$$100 \left(\frac{T - 3·73\ N - 0·89\ F}{C - 3·73\ N_s} \right) = Y = -144.$$

This value for Y has, of course, no *practical* meaning, but when substituted in the following formula, gives :

$$\frac{100\ T - CY}{24} = X = 81 \text{ per cent.}$$

whence the *real* value of $Y = (100 - 81) = 19$ per cent.

[A preferable formula for Y is :

$$Y = 100 \left(\frac{3S + T - 15N}{3S_x + C - 15N_s} \right)$$

in which $S_x = 75$ for wheat and barley flours, 95 for arrowroot and maize starch, and 89 for rice flour.]

As these values are probably nearer the truth than the more approximate ones obtained above, it will be assumed that there is 80 per cent. cocoa matter (nib + shell) and 20 per cent. of maize starch, which when calculated to the original dry sample (by multiplying by $\frac{23}{100}$), gives :

Cocoa matter   18·4 per cent. and **Maize starch   4·6 per cent.**

The proportion of nib and shell are now calculated for 100 parts of cocoa matter, as follows :

From the *nitrogen** . 18·4 0·78 : : 100 . 4·23.

On reference to the curves on pp. 305–6 it will be seen that the value 4·23 corresponds to :

Shell . 33 per cent. and Nib 67 per cent.

In a similar manner from the *fibre* the values obtained are :

Shell . 26 per cent. and Nib . 74 per cent.

and from the *levigation* curve :

Shell . 30 per cent. and Nib . 70 per cent.

It may therefore be assumed that the true composition approximates to :

Shell . 30 per cent. and Nib 70 per cent.

which values, when calculated back to the original dry sample, give :

Shell   ·   5·5 per cent. and **Nib   12·9 per cent.**

The composition of the dry sample therefore is :

Cane sugar	48·0
Fat .	29·0
Maize starch	4·5
Cocoa nib	13·0
Cocoa shell	5·5
	100·0

* If large quantities of starch be present or if it be wheat, barley or rice starch, the nitrogen which they contain must be allowed for. In the present case, since maize starch contains only 0·14 per cent. of nitrogen (p. 308), the amount introduced by 5 per cent. (being only 0·007 per cent.) may be neglected.

BOTANICAL INDEX.

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